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THE DETERMINATION OF THE ACTIVITY COEFFICIENT
OF A VOLATILE COMPONENT IN A BINARY SYSTEM
BY GAS-LIQUID CHROMATOGRAPHY

A THESIS

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THE DETERMINATION OF THE ACTIVITY COEFFICIENT
OF A VOLATILE COMPONENT IN A BINARY SYSTEM
BY GAS-LIQUID CHROMATOGRAPHY

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NOTE TO THE USER OF THIS THESIS

The results of this thesis have been published by C. F. Chueh and W. T. Ziegler in A.I.Ch.E. Journal 11, No. 3, 508-512(1965) in which a revised theoretical analysis is given. The theoretical analysis made in the thesis assumed that $dK/dy = 0$. This assumption does not agree with the facts. In the published work cited above the assumption $dK/dy \neq 0$ is used and is found to give better agreement with the experimental results.

W. T. Ziegler
November 16, 1965

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LIST OF SYMBOLS

| | |
|---------------------------|--|
| A, A_{11} | defined by equation (101) |
| A_{12} | defined by equation (103) |
| a | defined by equation (41) |
| B_{11} | second virial coefficient of component 1 as defined by equations (42) and (43), ml./gm. mole |
| B'_{22} | defined by equation (117), ml./gm. mole |
| B_m | second virial coefficient defined by equation (48), ml./gm. mole |
| B_{12} | second virial coefficient defined by equation (49), ml./gm. mole |
| C, C_{11} | defined by equation (101) |
| C_{12} | defined by equation (102) |
| C' | constant |
| D_L | molecular diffusivity in liquid phase |
| dev. | deviation between $(y_2^0)_s$ and y_2^0 , expressed as $((y_2^0)_s - y_2^0)/(y_2^0)_s$ |
| e | base of natural logarithms |
| f_p | pressure correction factor as defined by equation (63) |
| f_{2L} | fugacity of component 2 in the liquid phase at T and P_m |
| f_{2L}^0, f_2^0 | fugacity of pure component 2 in the liquid phase at T and P_2^0 |
| f_{2V}, f_2 | fugacity of pure component 2 in the vapor phase at T and P_m |
| \bar{f}_{2V}, \bar{f}_2 | partial fugacity of component 2 in the vapor phase |

| | |
|-------------|--|
| G, G_p | number of moles of gas in vessel p |
| \bar{G} | total number of moles of gaseous phase inside a gas chromatographic column |
| K, K_2 | vapor-liquid equilibrium constant of solute |
| L_p | number of moles of liquid in vessel p |
| \bar{L} | total number of moles of liquid phase inside a gas chromatographic column |
| M_s | molecular weight of absorbing liquid, gm./mole |
| M_2 | molecular weight of solute, gm./mole |
| m_s | number of moles of absorbing liquid in each vessel |
| \bar{m}_s | total number of moles of absorbing liquid inside a chromatographic column |
| N_f | mole flow rate of the gaseous mobile phase, mole/sec. |
| N_f' | molal flow rate of dry helium stream, mole/sec. |
| N_1 | number of moles of component 1 |
| N_m | number of moles of the gaseous mobile phase which has passed through a gas chromatographic column when the concentration of the solute at the end of the column is maximum |
| N_p, N | number of moles of gas which has passed through vessel p |
| n | total number of the vessels a chromatographic column equivalent to (do not include the first vessel) |
| P | pressure, mm. Hg |
| P_f | pressure in the soap film flow meter, mm. Hg |
| P_o | pressure at the outlet of a gas chromatographic column, mm. Hg |

| | |
|-------------|---|
| P_m | total pressure inside a gas chromatographic column, mm. Hg |
| P_n | vapor pressure of water at t_m , mm. Hg |
| P_1 | pressure at the inlet of a gas chromatographic column, mm. Hg |
| P_s | pressure at the exit of the last saturator, mm. Hg |
| P^* | critical or pseudo-critical pressure, mm. Hg |
| P_d^0 | vapor pressure of diethylene glycol, mm. Hg |
| P_1 | pressure of component 1, mm. Hg |
| P_2 | pressure of component 2, mm. Hg |
| P_2^0 | vapor pressure of component 2, mm. Hg |
| $(P_2^0)_s$ | vapor pressure of component 2 at t_s , mm. Hg |
| \bar{P}_2 | partial pressure of component 2, mm. Hg |
| p_1 | saturated pressure of component 1 at reduced temperature = 0.7, mm. Hg |
| R | gas constant |
| s | volume of sample injected, microliter |
| T | absolute temperature, generally, means the temperature inside a gas chromatographic column, °K |
| T_A | defined by equation (119) |
| T^* | critical or pseudo-critical temperature, °K |
| T_r | reduced temperature |
| t | temperature, °C |
| t_1 | temperature in a gas chromatographic column, °C |
| t_f | temperature of the flow meter, °C |
| t_s | temperature of the water bath surrounding the saturators, °C |

| | |
|--------------------------|---|
| V_f | volumetric flow rate of gaseous mobile phase measured at the column temperature and exit pressure |
| V'_f | volumetric flow rate of dry helium stream at t_f and P_f |
| V'_{fw} | volumetric flow rate of water-saturated helium stream measured by the soap film flow meter at t_f and P_f |
| V_G | volume of gas in a vessel, milliliter |
| V_i | molal volume of component i , ml./gm. mole |
| V_L | volume of liquid in a vessel, milliliter |
| V_m | molal volume of a gaseous mixture, ml./gm. mole |
| V_N | retention volume defined by equation (1), milliliter |
| V_{2L} | molal volume of liquid component 2 at T , ml./gm. mole |
| V^* | critical molal volume, ml./gm. mole |
| \bar{V}_G | total volume of gas (vapor) phase inside a gas chromatographic column, milliliter |
| \bar{V}_L | total volume of liquid phase inside a gas chromatographic column, milliliter |
| \bar{V}_i | total volume of component i , milliliter |
| \bar{V}_m | total volume of a gaseous mixture, milliliter |
| v | defined by equation (15) |
| w_{11}, w_{22}, w_{12} | acentric factors of component 1, 2, or mixture of 1 and 2 |
| W_s | total weight of absorbing liquid inside a gas chromatographic column, gram |
| W_2 | weight of solute being adsorbed by the activated charcoal, gram |
| x | mole fraction of solute in the liquid phase |

| | |
|----------------|--|
| x_p | mole fraction of solute in the liquid phase in vessel p |
| x^o, x_2^o | mole fraction of solute present in the chromatographic column prior to the injection of the solute sample |
| y_p | y_p minus y^o |
| y | mole fraction of solute in the vapor phase |
| y_s | y_s minus y^o |
| y_s | concentration of solute in the vapor phase in the first vessel right after the injection of a sample into the vessel |
| y_p | mole fraction of solute in the vapor phase in vessel p |
| y^o, y_2^o | mole fraction of solute present in the carrier gas prior to the injection of the solute sample |
| $(y_2^o)_s$ | mole fraction of solute in the vapor phase of the saturator |
| Z_m | compressibility factor of gaseous mixture at T and P_m as defined by equation (59) |
| Z_o | compressibility factor of gaseous mixture at T and P_o as defined by equation (35) |
| Z_2^o | compressibility factor of component 2 at T and P_2^o as defined by equation (61) |
| Z^* | compressibility factor at T^* and P^* |
| Z_{lf} | compressibility factor of helium at T_f and P_f |
| GREEK ALPHABET | |
| ρ | density |
| ρ_L | moles per unit volume of liquid inside a column measured at the column temperature t_1 |

| | |
|---------------|--|
| P_G | moles per unit volume of gas inside a column measured at the column temperature t_1 and the column exit pressure P_o |
| ϕ | correction factor for the imperfection of the vapor phase |
| ϕ_s | correction factor for the imperfection of the vapor phase evaluated at t_s , P_s , and $(y_2^o)_s$ |
| γ_{sL} | activity coefficient of absorbing liquid in the liquid phase |
| γ_{2L} | activity coefficient of solute in the liquid phase |
| θ_R | apparent retention time, second |
| θ | time (beginning at the injection of a solute sample) |
| θ_D | length of the time during which the solute in the column exit stream was adsorbed by the activated charcoal, second |

SUMMARY

The activity coefficient of a volatile solute in a relatively non-volatile solvent is difficult to measure by the conventional static equilibrium method because of the low equilibrium concentration of the solvent in the vapor phase and similarly the low concentration of the solute in the liquid phase. A number of investigators (10, 11, 12, 15, 17, 19, 21) have measured the activity coefficient of a solute at infinite dilution in such a non-volatile solvent by the gas-liquid chromatographic (GLC) method. In this method the gas chromatographic column used is packed with firebrick particles coated with the non-volatile solvent. A small solute sample is carried through the column by a non-soluble carrier gas such as helium. The time required for the solute sample to pass through the column is measured. The vapor-liquid equilibrium constant, K_2 , and hence the activity coefficient may be calculated from the retention volume by the following equations:

$$V_N = \bar{V}_G + \frac{1}{K_2} \left(\frac{\rho_L}{\rho_G} \right) \bar{V}_L \quad (1)$$

and

$$\gamma_{2L} = \frac{K_2 P_m \phi}{P_2^0} \quad (2)$$

where V_N = retention volume, measured at the column temperature and the column exit pressure, and corrected for the effect of pressure gradient across the column.

\bar{V}_G = total volume of gas phase inside the column

\bar{V}_L = total volume of liquid phase inside the column

ρ_G = density of gas phase measured at the column temperature and column exit pressure, moles per unit volume

ρ_L = density of liquid phase measured at the column temperature, moles per unit volume

P_m = total pressure inside the column

P_2^0 = vapor pressure of solute at the column temperature

γ_{2L} = activity coefficient of the solute in the liquid phase

ϕ = correction factor for the imperfection of the vapor phase

The derivation of equation (1) is based on the assumptions that the sample size injected is small and no solute vapor is present in the non-soluble carrier gas prior to the injection of the solute. The activity coefficient measured by this method is the activity coefficient of the solute at infinite dilution.

The object of the present study is to extend the GLC method of measuring the activity coefficient of the solute in a binary system from infinite dilution through a measurable concentration range. To accomplish this purpose, a gaseous mixture of solute vapor and helium gas was used instead of pure helium (or other inert gas) as the carrier gas. After the column was flushed by the gaseous mixture for a sufficient length of time, the non-volatile solvent inside the column was saturated with the solute and hence an equilibrium state between the vapor phase and liquid phase was reached. Both phases contained a finite amount of solute. A small sample of the solute was injected into the column and its retention volume was measured. The activity coefficient calculated from the retention vol-

ume measured at such condition was the activity coefficient of the solute in a solution which contained a finite amount of solute. By varying the concentration of the solute in the vapor phase, activity coefficients at various concentrations of the binary solution were measured.

A new relation between the retention volume and the equilibrium constant was derived to take into account the presence of the solute in the carrier gas. The same theoretical plate model used by Martin and Synge (24) to develop equation (1) was used here. The resultant equation is:

$$V_N = \bar{V}_G + \left(\frac{\rho_L}{\rho_G}\right)\left(\frac{\bar{V}_L}{K_2}\right)\left(\frac{1 - y_2^0}{1 - y_2^0/K_2}\right) \quad (3)$$

where y_2^0 is the mole fraction of the solute present in the vapor phase. The same equation has been derived by Stalkup and Dean (26) from a rate process approach based on the assumption that the slug of solute sample injected maintains a constant composition when it is carried through the column by the carrier gas.

The activity coefficients of two binary systems were studied experimentally. The particular systems selected were chosen because of the availability of published phase equilibrium data. The activity coefficients of benzene in diethylene glycol were measured at three temperature levels: 50°C, 70°C, 90°C, covering concentration ranges of zero to 31.1 mole per cent, zero to 24.1 mole per cent, zero to 9.08 mole per cent of benzene in the liquid phase, respectively. The activity coefficients of n-hexane in 1,2,4 trichlorobenzene were studied at 30°C, covering a concentration range from zero to 39.8 mole per cent of n-hexane in the liquid

phase.

The activity coefficients of the solute measured by the GLC method agree well with those obtained by the static equilibrium method in the dilute concentration region. At infinite dilution the agreement appears to be within the experimental errors of the two methods. In the region of higher concentration (concentration of solute in the liquid phase greater than 5 per cent) activity coefficients obtained by the GLC method agree less well with those obtained by the static equilibrium method, the deviation ranges from 3 per cent to a maximum of 15 per cent. In all instances the activity coefficients determined by the GLC method were lower. In the system of diethylene glycol -- benzene where the activity coefficients of benzene at the three different temperature levels, 50°C, 70°C, 90°C, have been studied, the deviation between the results obtained by the GLC method and the static equilibrium method is found to decrease with the increase of column temperature.

The effect of the sample size on the retention time was also studied. Based on both the analytical analysis and the experimental results, the relation between the retention time and the solute sample size is found to be closely related to the equilibrium constant, K_2 , and the mole fraction of the solute in the vapor phase, y_2^0 .

All the activity coefficients reported have been corrected for the effect of sample size as well as the effect of the imperfection of the vapor phase.

CHAPTER I

INTRODUCTION

While the gas-liquid equilibrium of mixtures of hydrocarbons of comparable volatility has been frequently investigated, few investigations of mixtures of hydrocarbons of widely different molecular size and volatility have been made. The equilibrium data of the latter type are essential to the absorption and stripping processes. Engineers in their process design still have to depend on so-called "K" values which are obtained by either assuming the ideal behavior of the solution or by a certain empirical correlation. A literature survey was made which covered 1) Chemical Abstracts from 1946 to 1958, 2) Industrial and Engineering Chemistry from 1955 to 1958, 3) Vapor-Liquid Equilibrium Data compiled by Chu et al. (1), and by Hala et al. (2) covering up to 1954 and 1957 respectively, and 4) Engineering Data Book (3) by Natural Gasoline Association of America Equilibrium Ratio Committee covering "the past ten or fifteen years" back from 1955. The search revealed little available data on the binary systems of light and heavy hydrocarbons. The system of methane and decane has been studied by Reamer et al. (4). Methane and Kensol 16 (C-16) was studied by Rzasa (5) up to 250°F and 25,000 lb/in². The binary systems of n-pentane with C₁₆, C₁₈, C₂₂, C₂₄ and n-heptane with C₁₉, C₂₃ were studied by Nederbragt and De Jong (6) at temperatures of 245.5 to 357°C. Kirkbride and Bertetti (7) studied the equilibrium relation of C₁ and C₅ in the two types of absorption oil at 85°F with the pressure in the range from 125 to 3100 psia. Mertes and Colburn (8) made

a comprehensive study of the binary systems of various isomers of butane with furfural covering the range of 100 to 200°F at pressures up to 100 psi.

The difficulties encountered in the study of such systems of widely different volatilities are the low-equilibrium concentration of the non-volatile component in the vapor phase and similarly the low concentration of the high-volatile component in the liquid phase. The error inherent in measurements made in such a low concentration range makes the activity coefficient calculated from them unreliable.

Martin (9), one of the inventors of Gas-Liquid Chromatography (GLC), first suggested that the measurement of retention volume of GLC provides a rapid means for the determination of the activity coefficient at infinite dilution for a binary system when a liquid of low volatility is involved. A substantial amount of work dealing with such measurements has been reported since then. Porter et al. (10) determined the partition coefficients of hydrocarbons and alcohols in diisodecyl phthalate by employing the latter as the stationary liquid of a gas-liquid chromatographic column. Some of the data obtained have been compared with those from direct equilibrium measurements and the results agree favorably. Keulemans (11) calculated activity coefficients at infinitely dilute concentration for a number of aliphatic and aromatic volatile hydrocarbons in various non-volatile hydrocarbons (C_{16} to C_{30}), diisodecyl phthalate, poly-alkylene glycol, etc.

Kwantes and Rijnders (12) summarized Keulemans' results and reported additional activity coefficient data at infinite dilution for systems such as volatile hydrocarbons in 1,2,4-trichlorobenzene and oxyge-

nated solutes in n-hexadecane, diisodecyl phthalate, poly-alkylene glycol, etc. They compared the values obtained by GLC with those calculated by the empirical relation of Brønsted and Koefoed, and the experimental static equilibrium data of Pierotti et al. (13), and Neckel and Kohler (14). Good agreement was reported. An extension of the GLC method to solvents of relatively higher volatilities by pre-saturating the carrier gas with vapor of the solvents, was also mentioned and the activity coefficient of the system such as n-pentane and n-octane had been determined successfully by Kwantes and Rijnders (12).

Hardy (15) calculated activity coefficients of various halogenated hydrocarbons in phthalates and silicone fluid from the retention volume data which he reported in a previous paper (16). Mellado and Kobayashi (17) obtained the vapor-liquid equilibrium constants of the systems of n-butane in n-dodecane and C_4 hydrocarbons in furfural by GLC; the results compare favorably with the NGAA values and values obtained by Mertes and Colburn (18) from the static equilibrium measurement. Adlard et al. (19) measured activity coefficients of benzene and cyclohexane in dinonyl phthalate by GLC method. A correction was made to account for the imperfection of the vapor phase. The activity coefficient of benzene was compared with that obtained by Ashworth (20) on the static equilibrium of the same system and good agreement was found. Everett and Stoddart (21) measured the activity coefficients of eight hydrocarbons at infinite dilution in dinonyl phthalate at 30°C by GLC. Their results, after being corrected for the imperfection of the vapor phase, agree within 1% of the extrapolated static equilibrium value measured by Ashworth (20). They pointed out that the correction for the gas imperfection used by Adlard

et al. (19) was in error.

All the reported activity coefficients discussed above which were determined by GLC method were measured in the range where the concentration of solute is very small, or so-called infinite dilution. These activity coefficients have only limited value in engineering practice. In absorption or distillation processes the concentration of solute involved is finite and the activity coefficient often is strongly dependent on the concentration. Besides, although good agreement between the activity coefficients at infinite dilution measured by the GLC and static equilibrium methods are often claimed, the validity of the GLC method is still frequently questioned. For example, Funk and Houghton (22) in their recent paper, based on a new approach to the mechanism of gas chromatography, suggested that the activity coefficient measured by the GLC should be multiplied by a correction factor which takes into account the "depth of penetration of solute in the liquid film". Their experimental results show that correction factor varies from 0.6 to 0.9, depending on the thickness of the liquid film. Because the accuracy of the conventional static equilibrium method decreases rapidly with the dilution, in order to compare the results obtained by the GLC method with those obtained by the static equilibrium measurement, a one-constant Margules equation was generally employed by the authors cited above to extrapolate the static equilibrium data measured at relatively higher concentration to the infinite dilution. Certain assumptions are involved in the Margules equation. No rigorous comparison between the results by the GLC method and static equilibrium methods can be made unless some of the measurements of activity coefficients by the GLC method are carried out in the same finite

concentration range where the static equilibrium measurement can also be carried out.

The object of the present investigation is to study the possibility of extending the GLC method of measuring the activity coefficient of the solute in a binary system from infinite dilution through a measurable concentration range. The basic principle employed, originally suggested by Stalkup and Kobayashi (23), is the mixing of an inert carrier gas with a certain amount of solute vapor. If the gas chromatographic column is flushed by the carrier gas for a sufficient length of time, the liquid phase inside the column will be saturated by the solute and hence an equilibrium state between the vapor phase (carrier gas) and liquid phase will be reached. Both phases contain a finite amount of solute. Under such a condition, if a small sample of the solute is injected into the column and its retention volume can be measured, the activity coefficient, which can be calculated from the retention volume, will be the activity coefficient of solute at the specific concentration instead of at infinite dilution. The significance of such a study is twofold: 1) In the finite concentration range, a direct comparison between the results obtained by the GLC method and those obtained by the static equilibrium methods is possible without the need of extrapolation. The accuracy and limitation of the GLC method then may be more rigorously examined; 2) The usefulness of GLC method in the measurement of activity coefficients will be greatly increased if the method covers a greater concentration range.

Many activity coefficients reported at infinite dilution measured by the GLC method (11, 12, 15, 17, 22) have been calculated on the basis that the vapor phase behaved as an ideal gas. In the cases where the im-

perfection of vapor phase was taken into account (19, 21) correction formulae based on different assumptions were used. The correction is essential if the data obtained by the GLC method are to be compared with data obtained by static equilibrium measurements. Special care was taken in the present study to determine a proper correction factor for vapor phase imperfection which should be applicable both at infinite dilution and in the finite concentration region.

CHAPTER II

THEORY

The Basic Mechanism of a Gas-Liquid Chromatographic Column.--A gas-liquid chromatographic column may be considered as a packed absorption tower in miniature. It consists of a mobile gaseous stream which percolates through a fixed bed coated with a non-volatile absorbing liquid. The basic difference between a chromatographic column and an absorption tower is that the latter, in general, is a continuous steady-state operation whereas in the former case the solute to be absorbed is introduced as a batch. The solute, in small quantity, is injected intermittently into the continuously flowing non-soluble carrier gas stream inside the chromatographic column and a concentration profile, which is both a function of distance and time, is developed. To study the relation between the retention time of the moving concentration profile inside the column and the vapor-liquid equilibrium constant of the solute involved, a theoretical plate model was suggested by Martin and Synge (24) the inventors of the liquid partition chromatographic column. Theory developed by this model was further treated by Klinkenberg and Sjenitzer (25), and Keulemans (11). All these authors arrived at the same relation between the vapor-liquid equilibrium constant and traveling time (expressed as the retention volume) of the peak concentration of solute passing through the column when the amount of the solute injected is small. This relation, which has become one of the fundamental laws in the field of gas-liquid chromatography is

$$V_N = \bar{V}_G + \frac{1}{K} \left(\frac{\rho_L}{\rho_G} \right) \bar{V}_L \quad (1)$$

where V_N = retention volume of the peak concentration of the solute band, expressed as the volume of the mobile gaseous phase at column temperature and column exit pressure, which has passed through the column from the time of injection to the appearance of the peak concentration of the solute at the end of the column. It should be corrected for the effect of pressure gradient across the column when the pressure gradient is appreciable.

\bar{V}_G = total volume of the gas inside the column

\bar{V}_L = total volume of the liquid inside the column

ρ_L = moles per unit volume of liquid inside the column measured at the column temperature

ρ_G = moles per unit volume of gas inside the column measured at the column temperature and column exit pressure

K = vapor-liquid equilibrium constant of the solute

Equation (1) was derived by assuming that the size of injected sample is small and that no solute vapor is present in the non-soluble carrier gas prior to the injection of the solute sample. The equilibrium constant, K , measured at this condition is the equilibrium constant of the solute at infinite dilution.

For this study a new relation between the retention volume and the equilibrium constant had to be derived to describe the more general case where a finite amount of solute is present in both the carrier gas stream and the absorbing liquid prior to the injection of the solute sample.

The equilibrium constant measured under such conditions is the equilibrium constant of the solute in a solution which contains a finite amount of solute.

In this derivation the same theoretical plate model used by Martin and Synge (24) is employed. In this model, a packed column is considered to be one composed of a number of "equilibrium stages". An "equilibrium stage" is called "H.E.T.P." (height equivalent to a theoretical plate) by Martin and Synge (24), "contacting stages" by Klinkenberg and Sjenitzer (25), and "equilibrium absorption vessel" by Keulemans (11). All these terms essentially have the same meaning that the average liquid concentration in an "equilibrium stage" is in equilibrium with the mobile gaseous phase leaving the stage. The number of the "equilibrium stages" for a column is not arbitrarily defined, but depends on the length and "efficiency" of the column in the same sense as the number of equivalent theoretical plates in a fractionating column or "H.E.T.P." in a packed absorbing tower. Other assumptions of the "theoretical plate model", also made in this derivation, are

- 1) No transfer of solute occurs from plate to plate by diffusion.
- 2) The solute sample injected is so small that the physical properties of both the gaseous and liquid phases remain essentially constant before and after the injection of the solute. One of these physical properties is the vapor-liquid equilibrium constant of the solute in the absorbing liquid.
- 3) The whole column is at a uniform temperature and under a uniform pressure, the pressure gradient required for flow being negligible.
- 4) The absorbing liquid is non-volatile.

Keulemans' (11) term "equilibrium absorption vessel" will be used rather than "equilibrium stage" and other symbols and mathematical treatment will be similar to Keulemans' (11) where they are applicable. However, all the quantities involved will be on mole basis rather than on volume basis which was conventionally used by all of the previous authors (11), (24), (25). In the absence of chemical reactions, the mole basis is equivalent to the mass basis which is more logical than the volume basis for the performance of a material balance.

In the theoretical plate model, a gas-liquid chromatographic column is considered to be a device in which a number of identical equilibrium absorption vessels, numbered 0, 1, 2, ..., p, ... are linked together with each vessel containing m_s^1 moles of the non-volatile absorbing liquid. A mobile phase which contains y^0 mole fraction of solute vapor mixed with carrier gas continuously percolates through the liquid phase and carries the vapor above the liquid from one vessel to another. After a sufficient length of time has elapsed an equilibrium condition is reached between the vapor and liquid phases of each vessel as indicated by uniform concentrations of solute in the vapor phase and liquid phase from vessel to vessel. The mole fractions of solute in the liquid phase and vapor phase of any vessel are x^0 and y^0 , respectively. At equilibrium

$$y^0 = Kx^0 \quad (2)$$

where K is the equilibrium constant at column temperature t_1 , column pressure p_m and concentration x^0 .

¹. All symbols are defined in the List of Symbols.

Assuming a small amount of solute is injected into the vapor phase of the first vessel, the previous static equilibrium condition is disturbed and a new form of dynamic equilibrium condition is established. As pictured in Fig. 1, an infinitesimal amount, dN_{p-1} moles, of mobile gas which is transferred from vessel $p-1$ into vessel p carries with it $y_{p-1}dN_{p-1}$ moles of the solute, while dN_p moles of mobile gas carries $y_p dN_p$ of the solute from vessel p into vessel $p+1$. An overall material balance around the vessel p yields:

$$dN_{p-1} - dN_p = dG_p + dL_p \quad (3)^1$$

The material balance of the solute around vessel p gives:

$$y_{p-1}dN_{p-1} - y_p dN_p = d(G_p y_p) + d(L_p x_p) \quad (4)$$

where L_p and G_p are the moles of gaseous and liquid phases in vessel p , and x_p and y_p are the mole fractions of the solute in the liquid phase and vapor phase in vessel p , respectively. y_p is in equilibrium with x_p , thus

$$y_p = Kx_p \quad (5)$$

¹In the original theoretical plate model suggested by Martin and Synge (24), and also in the further treatments done by others (11), (25), the right side of the equation (3) has been assumed to be zero. This assumption is permissible when the amount of the solute injected is small and no solute is present in the column and in carrier gas stream prior to the injection of the solute. In the case where a finite amount of solute vapor is present in the carrier gas all the time in addition to the trace solute which is injected intermittently, neglecting the terms in the right side of the equation (3) will introduce serious errors, especially, when the solute content in the carrier gas stream is high.

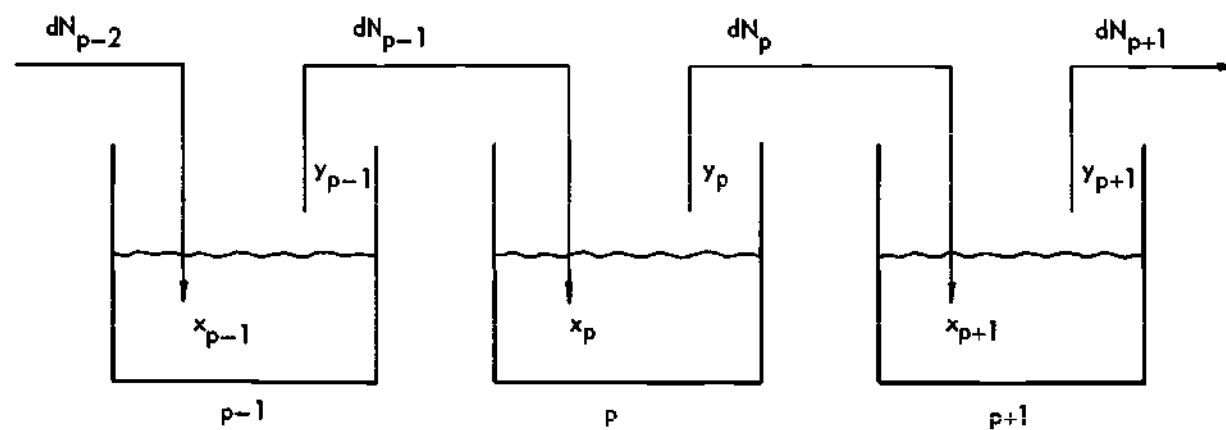


Figure 1. Equilibrium Absorption Vessels.

If equations (3), (4), and (5) are combined to eliminate dN_{p-1} and x_p then

$$(y_{p-1} - y_p)dN_p = (G_p + \frac{L_p}{K})dy_p + (\frac{y_p}{K} - y_{p-1})dL_p + (y_p - y_{p-1})dG_p \quad (6)$$

Based on a material balance of the absorbing liquid in each vessel, L_p is related to x_p by the following relation

$$L_p = \frac{m_s}{1 - x_p} = \frac{Km_s}{K - y_p} \quad (7)$$

then

$$dL_p = \frac{Km_s}{(K - y_p)^2} dy_p \quad (8)$$

By substituting these two equations into equation (6) it becomes

$$dN_p = \left\{ G_p + \frac{m_s((K - y_p) + y_p - Ky_{p-1})}{(K - y_p)^2} \right\} \left(\frac{dy_p}{y_{p-1} - y_p} \right) - dG_p \quad (9)$$

Since the amount of the solute sample injected is assumed to be small, the change of the concentration of the solute inside each vessel after the injection is small too, so is the change of the number of the moles of gas in vessel p . Mathematically, the above statements can be expressed as

$$dy_p \longrightarrow 0 \quad (10)$$

$$dG_p \longrightarrow 0 \quad (11)$$

$$y_{p-1} - y_p \longrightarrow 0 \quad (12)$$

or
$$y_{p-1} \approx y_p \approx y^0 \quad (13)$$

when $dy_p \rightarrow 0$ and $(y_{p-1} - y_p) \rightarrow 0$, $(\frac{dy_p}{y_{p-1} - y_p})$ is still a finite value in comparison to dG_p ; therefore, dG_p can be dropped since it is negligible compared to the other terms. Then upon substitution of equation (13) into equation (9), the latter equation becomes

$$dN = \left[G + \frac{m_s K(1 - y^0)}{(K - y^0)^2} \right] \frac{dy_p}{y_{p-1} - y_p} \quad (14)$$

The subscript p of G_p and N_p can be dropped in equation (14) because when the amount of sample injected is small, the variations of these two quantities between any two vessels are so small compared to G and N themselves that they are negligible¹.

Equation (14) can be put into a simpler form by defining

$$v = \frac{N}{G + \frac{m_s K(1 - y^0)}{(K - y^0)^2}} \quad (15)$$

where N is the number of moles of mobile gaseous stream which has passed through vessel p at time θ . Hence

$$dv = \frac{dN}{G + \frac{m_s K(1 - y^0)}{(K - y^0)^2}} \quad (16)$$

¹ However, in equation (4) N_{p-1} and N_p can not be assumed to be equal because the difference of N_{p-1} and N_p is not negligible in comparison to the difference of y_{p-1} and y_p .

By substituting equation (16) into equation (14), the latter is simplified to

$$\frac{dy_p}{dv} = y_{p-1} - y_p \quad (17)$$

By defining

$$Y_{p-1} = y_{p-1} - y^0 \quad (18)$$

$$Y_p = y_p - y^0 \quad (19)$$

the variables in the equation (17) can be replaced by

$$\frac{dY_p}{dv} = Y_{p-1} - Y_p \quad (20)$$

Solving equation (20) with the following initial condition: at $\theta = 0$ ($N = 0$, also $v = 0$), for all vessels except the first, $y_p = y^0$, and $Y_p = 0$, while for the first vessel (numbered as the vessel 0) $y_0 = y_s$, and $Y_0 = y_s - y^0 = Y_s$, we obtain

$$Y_p = Y_s \left(\frac{e^{-v_p}}{p!} \right) \quad (21)$$

The integration of equation (20) to obtain equation (21) is presented in Appendix I.

Equation (21) gives the concentration profile of a small solute sample which is carried through the gas chromatographic column continuously by a mobile gaseous stream. The concentration (Y_p) is a function of the time (expressed as the moles of gas which have passed through the

column, N or v) as well as distance (expressed by the number of the vessel, p) inside the column.

The maximum concentration of solute occurs in vessel p when

$$\frac{dY_p}{dv} = 0 \quad (22)$$

By combining equations (20) and (22),

$$Y_{p-1} = Y_p \quad (23)$$

and substituting the resultant equation (23) into equation (21) to obtain

$$\frac{v^{p-1}}{(p-1)!} = \frac{v^p}{p!} \quad (24)$$

yields

$$v = p \quad (25)$$

Equation (25) shows that for any vessel p , the maximum concentration occurs when v is equal to p .

The number of moles of gas which has passed through vessel p when maximum concentration occurs in this vessel is obtained by combining equation (25) and equation (15).

$$(N)_{y=\max. \text{ at } p} = p \left[G + \frac{m_s(1 - y^0)K}{(K - y^0)^2} \right] \quad (26)$$

The gas chromatographic column is considered to be composed of $(n + 1)$ equilibrium vessels. The last vessel is the n th vessel because the

first vessel was numbered zero. The number of moles of gas which has passed through the last vessel when the maximum concentration occurs at the end of the chromatographic column may be obtained by replacing p with n in equation (26).

$$(N)_{y=\max. \text{ at } n} = n \left[G + \frac{m_s(1 - y^0)K}{(K - y^0)^2} \right] \quad (27)$$

By assuming n is sufficiently large¹ that

$$n = n + 1 \quad (28)$$

the following equations are obtained:

$$nG \doteq (n + 1)G = \bar{G} \quad (29)$$

$$nm_s \doteq (n + 1)m_s = \bar{m}_s \quad (30)$$

Using these equations, equation (27) becomes

$$(N)_{y=\max. \text{ at } n} = \bar{G} + \frac{\bar{m}_s K(1 - y^0)}{(K - y^0)^2} \quad (31)$$

where \bar{G} and \bar{m}_s are the moles of the gaseous phase and moles of non-volatile absorbing liquid inside the whole column, respectively.

¹The method of calculating number of theoretical plates (or equilibrium absorption vessels) from the chromatogram has been described by Martin and Synge (24) and Keulemans (11). The number of plates is in general over 30 per foot of column length. The number of plates of the two columns (3 feet each) used in the present study varied from 150 to 400, depending on the column temperature, flow rate, etc.

In order to compare equation (31) with equation (1), equation (31) is converted from mole units to the more conventional volume units:

$$\rho_G V_N = \rho_G \bar{V}_G + \frac{\bar{m}_s(1 - y^o)}{K(1 - x^o)^2} \quad (32)$$

Based on the material balance of the absorbing liquid, we obtain

$$\bar{L} = \rho_L \bar{V}_L = \frac{\bar{m}_s}{1 - x^o} \quad (33)$$

where \bar{L} = total number of moles of liquid phase inside the column.

By substituting equation (33) into equation (32) and re-arranging it, equation (32) becomes

$$V_N = \bar{V}_G + \frac{1}{K} \left(\frac{\rho_L}{\rho_G} \right) \bar{V}_L \left(\frac{1 - y^o}{1 - x^o} \right) \quad (34)$$

Comparing equation (34) with equation (1), it is seen that equation (1) is merely a special case when y^o and x^o , the concentration of solute in the carrier stream and absorbing liquid, are zero prior to the injection of the trace amount of the solute.

By defining

$$\rho_G = \frac{P_o}{Z_o RT} \quad (35)$$

where P_o = pressure at the column exit, mm. Hg

Z_o = compressibility factor at temperature T and pressure P_o

T = column temperature, °K

R = gas constant

and substituting equation (35) into equation (34), equation (34) becomes:

$$V_N - \bar{V}_G = \frac{Z_o R T \bar{M}_s K (1 - y^o)}{P_o (K - y^o)^2} \quad (36)$$

Equation (36), which was first derived here from the theoretical plate model, has been derived by Stalkup and Dean (26) from the rate process approach. They assumed the point equilibrium between liquid and gas throughout the column and a band of constant composition moving through the column, although they pointed out "in reality the composition of the solute band continuously changes from entrance to exit of the column". In other words, they have assumed that the chromatographic column is so efficient that it is equivalent to an infinite number of theoretical plates in a finite length. Both the rate and plate models arrive at the same relation between the equilibrium constant and the retention volume of the peak concentration. This agreement results rather incidentally from the fact that the retention volume of the peak concentration is independent of the number of theoretical plates the column is equivalent to, as long as the number is sufficiently large, as it is shown in equations (29), (30), and (31). Consequently, the correct relation results even if in the case of the simplified rate model the number of plates much greater than those which can be practically realized has been assumed. However, no such liberty is allowed in predicting the concentration profile of solute other than the peak point. The rate model by Stalkup and Dean (26) does not predict the same concentration profile expressed by equation (21) which is a Poisson distribution in agreement with the commonly seen experimental

chromatograms.

By re-arranging equation (31) and adding the subscript 2 to K and y to designate solute to be consistent with the symbols used in the later chapters, equation (31) becomes:

$$\frac{K_2}{(K_2 - y_2^0)^2} = \frac{(N_m - \bar{G})M_s}{(1 - y_2^0)W_s} \quad (37)$$

where $N_m = N_{y=\text{max. at } n}$

= the number of moles of gaseous mobile phase which has passed through a gas chromatographic column when the concentration of the solute at the end of the column is maximum.

M_s = molecular weight of the absorbing liquid, gram/mole

$W_s = M_s \bar{m}_s$

= total amount of the liquid phase inside the column, gram

In the derivation of equation (37), an assumption has been made that the whole gas chromatographic column is under a uniform pressure. In any practical gas chromatographic column, a pressure gradient is required to move the gas phase through the column. To account for the effect of the change of the density throughout the column due to the pressure gradient, a correction factor has been derived by James and Martin (27), based on the assumptions that 1) the gas flow in the column is a laminar flow¹, and that 2) the gas phase behaves as an ideal gas. For a column

¹The Reynolds number of the gas flow inside the gas chromatographic column was below 120 in the velocity range covered by the present study. Experimental data summarized by Brown (28) show that flow in a porous medium changes from the laminar flow to the turbulent flow when the Reynolds number is greater than 400.

with pressure gradient, equation (37) thus is modified as

$$\frac{K_2}{(K_2 - y_2^o)^2} = \frac{(N_m - \bar{G})M_s f_p}{(1 - y_2^o) W_s} \quad (38)$$

$$f_p = \left(\frac{3}{2}\right) \frac{(P_1/P_o)^2 - 1}{(P_1/P_o)^3 - 1} \quad (39)$$

where P_1 is the column inlet pressure and P_o is the column exit pressure. When $1.0 \leq (P_1/P_o) \leq 1.025$, as in the pressure range involved in the present study, the correction factor falls in the range of 0.99 to 1.00.

If equation (38) is solved for K_2 , it becomes

$$K_2 = \frac{1}{2}(2y_2^o + a) + \frac{1}{2} \left[(2y_2^o + a)^2 - 4(y_2^o)^2 \right]^{\frac{1}{2}} \quad (40)$$

where

$$a = \frac{(1 - y_2^o)W_s}{(N_m - \bar{G})M_s f_p} \quad (41)$$

In equation (40) only the positive root is chosen because if the negative root is chosen K_2 becomes zero at $y_2^o = 0$, which apparently is a trivial answer.

The activity coefficient of the solute in the liquid phase is defined as

$$\gamma_{2L} = \frac{\bar{f}_{2V}}{x_2^o f_{2L}} \quad (42)$$

and a correction factor for the imperfection of the vapor phase is defined as:

$$\phi = \frac{\bar{f}_{2V} P_2^0}{y_2^0 P_m f_{2L}} \quad (43)$$

Combining equations (42) and (43) to eliminate (\bar{f}_{2V}/f_{2L}) the following equation results

$$\gamma_{2L} = \left(\frac{y_2^0 P_m}{x_2^0 P_2^0} \right) \phi \quad (44)$$

$$= \left(\frac{K_2 P_m}{P_2^0} \right) \phi \quad (45)$$

where γ_{2L} = activity coefficient of solute dissolved in the non-volatile absorbing liquid

\bar{f}_{2V} = partial fugacity of the solute vapor at column temperature, T , column pressure, P_m , and solute concentration, y_2^0

f_{2L} = fugacity of the pure solute liquid at column temperature, T , and column pressure, P_m

P_m = total pressure inside the column

P_2^0 = vapor pressure of the solute at the column temperature, T

Through equations (40), (41), and (45), γ_{2L} is expressed as a function of P_m , T , P^0 , z_m , ϕ , $(N_m - \bar{G})$ and y_2^0 . T , the column temperature, and P_m , the column pressure, are the measurable quantities. P_2^0 , the vapor pressure of solute can be determined from the column temperature if a suitable temperature and vapor pressure relation is known. The determi-

nation of ϕ , $(N_m - \bar{G})$ and y_2^0 is discussed in subsequent sections.

Correction for the Imperfection of the Vapor Phase.--The correction factor ϕ , defined by equation (43), primarily is a measure of the non-ideality of the vapor (gaseous) phase involved in the vapor-liquid equilibrium study. (ϕ includes also a minor correction term which accounts for the effect of the difference of the total pressure and vapor pressure on the liquid phase. This minor correction term is the only correction which would be necessary if the gaseous phase behaved ideally.) To determine the quantity, an experimental P-V-T-y relation or an equation of state which can represent real gas with reasonable accuracy is required. In this study a virial form of an equation of state truncated after the second term was assumed. For a binary system the equation can be written for each pure component and their mixture as

$$P_1 = \frac{N_1 RT}{\bar{V}_1} \left(1 + \frac{N_1 B_{11}}{\bar{V}_1} \right) \quad (46)$$

$$P_2 = \frac{N_2 RT}{\bar{V}_2} \left(1 + \frac{N_2 B_{22}}{\bar{V}_2} \right) \quad (47)$$

$$P_m = (N_1 + N_2) \left(\frac{RT}{\bar{V}_m} \right) \left[1 + \frac{(N_1 + N_2) B_m}{\bar{V}_m} \right] \quad (48)$$

where

$$B_m = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \quad (49)$$

The determination of the second virial coefficients, B_{11} , B_{22} ,

and B_{12} is discussed in the latter part of this section.

In order to express ϕ in terms of the variables of the equation of state, the following thermodynamic relations are introduced:

Beattie and Stockmayer (29) have shown that for a pure gas:

$$RT \ln f_2^o = \int_{\bar{V}_2}^{\bar{V}_2^\infty} \left[\left(\frac{\partial P_2}{\partial N_2} \right)_{\bar{V}_2, T} - \frac{RT}{\bar{V}_2} \right] d\bar{V}_2 - RT \ln \frac{\bar{V}_2}{N_2 RT} \quad (50)$$

and for component 2 in a gaseous mixture

$$RT \ln \bar{f}_{2V} = \int_{\bar{V}_m}^{\bar{V}_m^\infty} \left[\left(\frac{\partial P_m}{\partial N_2} \right)_{\bar{V}_m, T} - \frac{RT}{\bar{V}_m} \right] d\bar{V}_m - RT \ln \frac{\bar{V}_m}{N_2 RT} \quad (51)$$

Because by definition $\bar{V}_m = \sum N_i \bar{V}_i$ (52)

and $y_2 = \frac{N_2}{\sum N_i}$ (53)

Equation (51) may be changed to:

$$RT \ln \bar{f}_{2V} = \int_{\bar{V}_m}^{\bar{V}_m^\infty} \left[\left(\frac{\partial P_m}{\partial N_2} \right) - \frac{RT}{\bar{V}_m} \right] d\bar{V}_m - RT \ln \frac{\bar{V}_m}{y_2 RT} \quad (54)$$

Equation (50) is subtracted from equation (54) to obtain

$$\ln \frac{\bar{f}_{2V}}{y_2 f_2^o} = \frac{1}{RT} \int_{\bar{V}_m}^{\bar{V}_m^\infty} \left[\left(\frac{\partial P_m}{\partial N_2} \right) - \frac{RT}{\bar{V}_m} \right] d\bar{V}_m - \frac{1}{RT} \int_{\bar{V}_2}^{\bar{V}_2^\infty} \left[\left(\frac{\partial P_2}{\partial N_2} \right) - \frac{RT}{\bar{V}_2} \right] d\bar{V}_2 + \ln \frac{V_2}{V_m} \quad (55)$$

A minor correction for the pressure effect on the fugacity of solute in the liquid phase is made here to convert f_2^o (at P_2^o) to f_{2L} (at P_m).

$$RT \ln f_{2L} = RT \ln f_2^o + \int_{P_2^o}^{P_m} V_{2L} dP \quad (56)$$

Equation (56) is substituted into equation (55) to obtain

$$\begin{aligned} \ln \frac{\bar{f}_{2V}}{y_2 f_{2L}} = & \frac{1}{RT} \int_{\bar{V}_m}^{\bar{V}_m^\infty} \left[\left(\frac{\partial P_m}{\partial N_2} \right) - \frac{RT}{\bar{V}_m} \right] d\bar{V}_m - \frac{1}{RT} \int_{\bar{V}_2}^{\bar{V}_2^\infty} \left[\left(\frac{\partial P_2}{\partial N_2} \right) - \frac{RT}{\bar{V}_2} \right] d\bar{V}_2 \\ & + \ln \frac{V_2}{V_m} - \int_{P_2^o}^{P_m} V_{2L} dP \end{aligned} \quad (57)$$

where f = fugacity

\bar{f} = partial fugacity

N = number of moles

p = pressure

T = absolute temperature

R = gas constant

V = molal volume

\bar{V} = total volume

y = mole fraction in the vapor phase

Subscripts: 1, 2, ..., i = component 1, 2, ..., i

m = mixture of component 1, 2, ..., and i

L = liquid phase

V = vapor phase

Superscripts:

o = at the pressure equal to the vapor pressure of the pure component

$^\infty$ = at a very low pressure such that the gas may be considered as an ideal gas

By differentiating equations (46), (47), and (48), substituting the results into equation (57), and performing the integration, the following equation results:

$$\ln \frac{\bar{f}_{2V}}{y_2 f_{2L}} = \ln \frac{P_m}{P_2^o} + \ln \frac{Z_2^o}{Z_m} - 2(Z_2^o - 1) - \frac{V_{2L}}{RT} (P_m - P_2^o) + \frac{2P_m}{Z_m RT} (y_1 B_{12} + y_2 B_{22}) \quad (58)$$

Z_m is defined as:

$$Z_m = \frac{P_m \bar{V}_m}{(N_1 + N_2)RT} \quad (59)$$

Solving the quadratic equation (48) for \bar{V}_m and substituting it into equation (59), Z_m is found to be

$$Z_m = 0.5 + \left(0.25 + \frac{B_m P_m}{RT}\right)^{1/2} \quad (60)$$

Only the positive root is chosen because this root leads to unity when B_m is equal to zero for an ideal gas. Similarly,

$$Z_2^0 = \frac{P_2^0 \bar{V}_2}{N_2 RT} = 0.5 + \left(0.25 + B_{22} P_2^0 / RT\right)^{1/2} \quad (61)$$

The correction factor for the imperfection of the vapor phase has been defined as:

$$\phi = \left(\frac{\bar{F}_{2V}}{y_2 P_m}\right) \left(\frac{P_2^0}{f_{2L}}\right) \quad (43)$$

Substituting equation (43) into equation (58), the following final equation is obtained:

$$\ln \phi = \ln \frac{Z_2^0}{Z_m} - 2(Z_2^0 - 1) - \frac{V_{2L}}{RT} (P_m - P_2^0) + \frac{2P_m}{Z_m RT} (y_1 B_{12} + y_2 B_{22}) \quad (62)$$

In addition to the assumption of the equation of state of the virial form, the following assumptions were made in the derivation of equation (62):

- 1) The volume of the liquid phase of component 2 (solute) is independent of pressure in the range of P_2^0 to P_m .
- 2) The vapor phase is a binary system which consists only of the carrier gas (component 1) and solute vapor (component 2). The vapor pressure of the absorbing liquid is assumed to be negligible.

In order to solve equation (62), the second virial coefficients of the inert carrier gas, solute vapor and their mixture are required. The second virial coefficient of helium (inert carrier gas) can be calculated from the constants of the Beattie-Bridgeman equation of state. Korvezee (30) calculated the second virial coefficient of benzene (solute) by integrating the derivative of heat capacity with respect to pressure and choosing the integration constant from the best available experimental values of second virial coefficients at 320°K. Techo (31) fitted a Berthelot type equation to the experimental data of the second virial coefficient of benzene. Both Korvezee's and Techo's equations agree well in the temperature range which was involved in the present study. Korvezee's equation was chosen. No experimental data are available for the second virial coefficients of mixtures of benzene and helium. As it is shown in Table 14 of Appendix III, at 50°C, B_{12} of the mixture of helium and benzene, estimated by mixture rules suggested by 1) Lorentz and Berthelot (32), 2) Guggenheim and McGlashan (33), and 3) Prausnitz and Gunn (34) varies from 22 to 51 ml./gm. mole. The Prausnitz and Gunn's rule is chosen in the present study because it has been shown to agree well with experimental data in the system of hydrogen and decane, which resembles the present system of helium and benzene as far as the ratio of molecular sizes of the two components involved is concerned.

The second virial coefficient of n-hexane (solute of the second system being studied) was calculated by the equation suggested by Pitzer and Curl (35) which is based on the principle of corresponding states. The value calculated at 30°C (- 1800 ml./gm. mole) agrees with the experimental value (- 1600 ml./gm. mole) given by Lambert et al. (36). Praus-

nitz and Gunn's (34) rule was used to calculate the R_{12} of helium and n-hexane.

Determination of Concentration of Solute in the Vapor Phase.--A gaseous mobile phase of constant composition was prepared by passing helium gas stream through saturators containing liquid solute maintained at a constant temperature. The gas stream coming out of the saturator was allowed to flow through the gas chromatographic column until a steady state was reached, as indicated by a thermistor detector which compared the concentrations of solute at the column input and output (see Chapter IV "Experimental Equipment"). At this point, the concentration of solute in the vapor phase of the column was equal to its concentration in the exit stream from the column. The concentration of solute in the exit stream was determined by the absorption of solute in the activated charcoal. The length of the absorption period, θ_D , was recorded by a stop timer and the volumetric flow rate of the solute-free helium coming out the exit of the absorption bottle was measured by a soap film flow meter (see Chapter IV, "Experimental Equipment"). The helium stream was saturated by the water vapor inside the soap film flow meter at temperature t_f and pressure P_f . The volumetric flow rate of helium at t_f and P_f can be converted from the wet basis (water saturated) to the dry basis by the following equation:

$$V'_f = V'_{fw} \left(\frac{P_f - P_n}{P_f} \right) \quad (63)$$

where V'_f = volumetric flow rate of water-saturated helium stream measured by soap film flow meter in ml./sec. at the temperature t_f

and the pressure P_f

V'_f = volumetric flow rate of dry helium gas at t_f and P_f

P_n = vapor pressure of water at t_f

The flow meter was maintained at room temperature, therefore, P_n (20 to 30 mm. Hg) was small compared to P_f (atmospheric pressure). Thus the helium-water vapor mixture can be assumed to be a perfect gas mixture in equation (63) with negligible error.

The volumetric flow rate of dry helium V'_f can be converted to molal flow rate of dry helium, N'_f , by the following equation:

$$N'_f = \frac{V'_f P_f}{Z_{1f} R T_f} \quad (64)$$

Z_{1f} which is the compressibility of helium gas at T_f and P_f can be evaluated by equation (61) after substituting B_{11} for B_{22} , T_f for T , and P_f for P_2^0 .

$$Z_{1f} = 0.5 + (0.25 + B_{11} P_f / R T_f)^{1/2} \quad (65)$$

The mole fraction of solute in the gaseous mobile phase, y_2^0 , thus can be calculated by the following equation:

$$\frac{y_2^0}{1 - y_2^0} = \frac{\frac{W_2}{M_2}}{N'_f \theta_D} \quad (66)$$

where W_2 = the number of the grams of solute adsorbed by the activated charcoal during the time period of θ_D

M_2 = molecular weight of solute, gram/mole.

θ_D = length of the time of adsorption, second.

Equation (66) is based on the assumption that the adsorption of solute by the activated charcoal was complete. This has been studied in this research for the case of benzene and activated charcoal.

1) The samples which were taken from the inlet and outlet of the adsorption bottle were analyzed by a gas chromatograph. The outlet contained less than 0.10 mole per cent benzene while the inlet stream contained 30 mole per cent benzene.

2) The mole fraction calculated by equation (64) was compared with that computed from the vapor pressure of benzene at the temperature of the saturator, based on the assumption that the saturation is complete. The deviation, in general, was less than 3 per cent of the computed value (see the section "Discussions of Experimental Results" of Chapter VI).

Determination of $(N_m - \bar{G})$ --- N_m has been defined as the number of the moles of the gaseous mobile phase which has passed through a gas chromatographic column from the time of the injection of the solute into the column to the appearance of the peak concentration of the solute at the end of the column; and \bar{G} is the number of moles of gas phase inside the column. By re-arranging equation (38) to the following form

$$N_m = \bar{G} + \frac{W(1 - y_2^o)}{K_2(1 - x_2^o)^2 M_s f_p} \quad (67)$$

it can be seen that \bar{G} is merely the N_m of a solute sample, such as air, with K_2 approaching infinity. $(N_m - \bar{G})$ thus can be obtained by simply measuring θ_R , the time interval between the appearance of the concentration peaks of air sample and solute sample which are injected

simultaneously, then multiplying it by N_f , the molal flow rate of the gaseous mobile phase.

$$N_m - \bar{G} = N_f \theta_R \quad (68)$$

θ_R is called "apparent retention time" in the field of gas chromatography. N_f is related to N'_f , the molal flow rate of dry helium gas, by the following equation:

$$N'_f = N_f(1 - y_2^o) \quad (69)$$

By combining equations (63), (64), (68), and (69), the working formula for the calculation of $(N_m - \bar{G})$ becomes:

$$(N_m - \bar{G}) = (V'_{fw}) \left(\frac{P_f - P_n}{Z_{1f} RT_f} \right) \left(\frac{1}{1 - y_2^o} \right) (\theta_R) \quad (70)$$

A sample calculation is presented in Appendix IV.

CHAPTER III

SYSTEMS AND MATERIALS

Two binary systems, diethylene glycol -- benzene and 1,2,4 trichlorobenzene -- n-hexane, dictated by the following reasons, were selected for the present study:

1) Relatively low vapor pressure of diethylene glycol and 1,2,4 trichlorobenzene: 1.2 mm. Hg at 90°C and 0.82 mm. Hg at 30°C, respectively.

2) Suitable volatility of benzene and n-hexane: 200 mm. Hg at 42.2°C and 31.6°C, respectively.

3) Phase equilibrium data of the two binary systems, obtained from static equilibrium measurements by Pierotti et al. (13) and Neckel and Kohler (14), were available for comparison.

The diethylene glycol used was supplied by Matheson Coleman and Bell Division of the Matheson Company, Norwood, Ohio, with the specification of B.P. 128-130°C/10 mm. Hg. Its refractive indices, measured in this laboratory, were $n_D^{25^\circ\text{C}} = 1.44535$ and $n_D^{20^\circ\text{C}} = 1.44710$, respectively. The latter value agrees well with $n_D^{20^\circ\text{C}} = 1.4472$ reported by Curme and Johnston (37). Analysis was made with a Perkin-Elmer¹ Vapor Fractometer using a "Q"² column at a temperature of 220°C. No impurities

¹. Perkin-Elmer Corporation, Norwalk, Connecticut.

². Apiezon "L" Grease coated on diatomaceous earth, maximum recommended temperature 325°C, supplied by Perkin-Elmer Corporation.

could be found.

The benzene used was Baker reagent grade with the normal boiling point specified as $80.1 \pm 0.2^\circ\text{C}$. This commercial reagent was recrystallized twice in this laboratory. The solid portion, which had a refractive index $n_D^{25^\circ\text{C}} = 1.49792$, the same value reported by the API project 44 (38), was retained. Analysis by the Perkin-Elmer Vapor Fractometer using a diethylene glycol column indicated that the purified benzene contained less than 0.02 weight per cent of impurities.

The 1,2,4 trichlorobenzene used was also supplied by Matheson Coleman and Bell Division of the Matheson Company, with the specification of M.P. 17°C . Analysis by the Perkin-Elmer Vapor Fractometer using a "Q"¹ column at 175°C indicated it contained five different trace impurities, amounting to a total of 1.5 weight per cent. After recrystallizing it for three times, the impurities were reduced to 0.5 weight per cent. The melting point of the purified product was determined as 16.8 to 16.9°C , which agrees well with the values given in the International Critical Tables (16.6°C) (39) and Neckel and Kohler (16.7°C) (14).

The n-hexane used was Phillips Petroleum Company's "pure-grade" with the specification of minimum 99 per cent purity. Analysis using a Perkin-Elmer "A"² column indicated that it contained less than 0.5 weight per cent impurities. Its refractive index measured by Hwa (40) was

¹. Apiezon "L" Grease coated on diatomaceous earth, maximum recommended temperature 325°C , supplied by Perkin-Elmer Corporation.

². Diisodecyl phthalate coated on diatomaceous earth, maximum recommended temperature 175°C , supplied by Perkin-Elmer Corporation.

$n_D^{20^\circ\text{C}} = 1.37491$ against $n_D^{20^\circ\text{C}} = 1.37486$ reported by API Project 44 (38). Some of the same lot of reagent which had been used in Hwa's investigation was used in the present study.

Helium was used as the inert carrier gas because of its inertness, its high thermal conductivity which provides high sensitivity for the thermistor detecting cell in the Perkin-Elmer Vapor Fractometer used in the study, and its low solubility in the liquid phase. The helium gas used was supplied by Marks Oxygen Company, Savannah, Georgia, with guaranteed purity of 99.99 per cent. A three-foot, 3/16-inch I.D. copper tubing, packed with adsorbent Molecular Sieve 13X, was installed in the outlet of the helium tank to remove any traces of moisture from the helium.

The experimental GLC columns used were prepared using particles of Johns-Manville¹ Firebrick C-22 as the inert solid support material. This material has been accepted by the workers in the field of gas chromatography as the most efficient support material because of its inertness and porous structure which provides great contact area even if the particles used are relatively coarse. The particles used were prepared by grinding Firebrick C-22, supplied by Johns-Manville Company. After carefully screening, the sieved 14 to 20 mesh size particles were washed with distilled water and then dried in a 300°C oven for three hours before being coated with diethylene glycol or 1,2,4 trichlorobenzene.

¹. Johns-Manville Company, 22 E. 40th Street, New York, New York.

CHAPTER IV

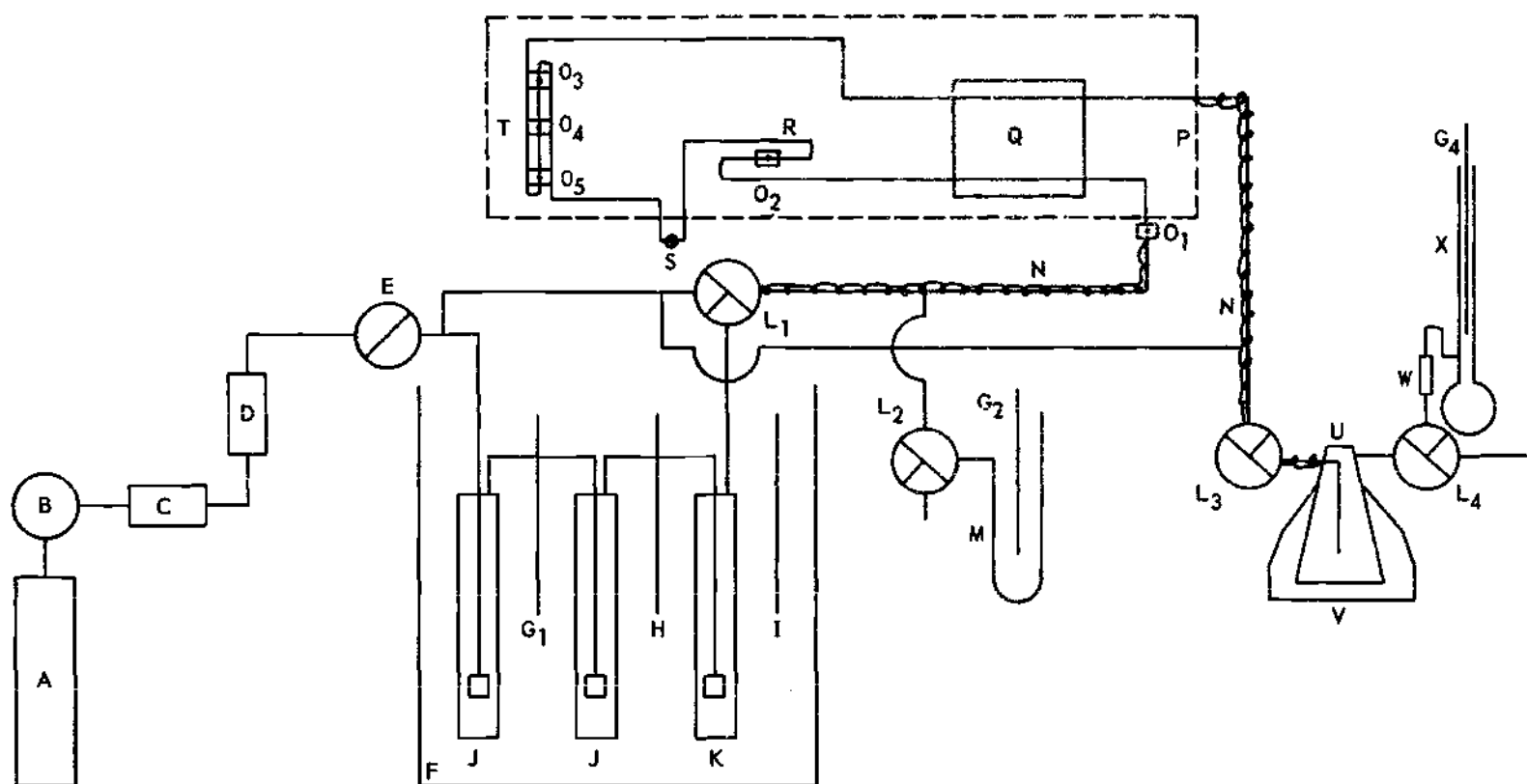
EXPERIMENTAL EQUIPMENT

The schematic diagram in Fig. 2 gives the general layout of the experimental apparatus. The apparatus consisted essentially of 1) a gas saturation system, including flow rate control valves, gas saturators, a de-entrainment trap and a constant temperature water bath, to prepare the carrier gas containing a known concentration of solute; 2) solute adsorption bottle and adsorbent regenerator; and 3) a gas-chromatographic unit including column, column oven and heating system, detector, and recorder. The design and function of each of these principal components, along with their associated measuring instruments, is discussed in detail below:

Gas Saturation System:

The carrier gas, containing a definite amount of solute vapor (benzene or n-hexane), was prepared by passing the helium gas stream through saturators (J)¹ containing liquid benzene or n-hexane. To assure that the exit gas had been saturated at the liquid temperature, three gas saturators, made of vertical tubes and fritted glass dispersers, were connected in series. The third one (K), containing no liquid initially, served primarily as a de-entrainment trap. All the three saturators were immersed in a ten gallon constant temperature water bath (F), manufactured by Wilkens-Anderson Company, Chicago, Illinois. The bath, consisting of a

¹. Letters refer to Fig. 2.



A - Helium Tank
 B - Pressure Regulator
 C - Molecular Sieve Moisture Adsorption Column
 D - Rotameter
 E - Pressure Reducing Needle Valve

F - Constant Temperature Water Bath
 G - Thermometer
 H - Stirrer
 I - Thermostat
 J - Saturator
 K - De-entrainment Trap

L - Three Way Valve
 M - Monometer
 N - Heating Coil
 O - Thermocouple
 P - Constant Temperature Column Oven
 Q - Detector

R - Pre-saturation Column
 S - Sample Injection Block
 T - Gas-Chromatographic Column
 U - Turner Adsorption Bottle
 V - Heater
 W - Humidifier
 X - Soap Film Flow Meter

Figure 2. Schematic Diagram of Equipment.

stirrer (H), a refrigerator and a heater both controlled by a mercury thermo-regulator (I), maintained a constant temperature ($\pm 0.05^{\circ}\text{C}$) over the range both above and below room temperature as measured by a 0.1°C subinterval mercury thermometer (G_1), which had been compared with a National Bureau of Standards certified 0.1°C subinterval mercury thermometer. The benzene-saturated helium which left the de-entrainment trap (K) was led by the copper tubing into the column oven (P). The temperature of the wall of the copper tubing was maintained at a temperature above the water bath temperature by an electrically heated coil (N) and fiber glass insulation to prevent the condensation of solute vapor in the carrier gas stream.

Adsorption Bottle:

In order to determine the concentration of solute in the carrier gas stream, (which is also the concentration of solute in the vapor phase of the gas chromatographic column) the gas leaving the column was led by the heated copper tubing into a Turner (41) adsorption bottle (U) filled with activated charcoal (Columbia, 8/14 mesh, Grade 6G). The flow rate of the solute-free helium leaving the adsorption bottle was measured by a soap film flow meter (X) which had been described by Keulemans (42). The product of the exit flow rate and length of adsorption time, measured by a Thompson electric stop timer, yielded the total volume of the solute-free helium passing through the adsorption bottle. This value must be corrected for the water vapor present in the soap film meter. To assure that the helium in the film flow meter was saturated by water vapor at the temperature at which the measurement was carried out, the Tygon tube (W) connecting the Turner adsorption bottle and soap film flow meter was

packed with coarse particles of Firebrick soaked with soapy water. The amount of solute being adsorbed was obtained by the difference between the weight of the Turner adsorption bottle (U) before and after the adsorption. A Fisher¹ chemical balance was used for weighing. The weights, Ainsworth class S, were calibrated individually by the supplier² with a maximum correction of 0.03 mg. marked for each weight. To regenerate the activated charcoal after adsorption, the Turner adsorption bottle (U) was purged by solute-free helium gas, by passing the saturators and column. The temperature of the Turner bottle was maintained at 380°F during the period of regeneration by an electrical heater (V).

Gas Chromatograph:

The diethylene glycol gas-chromatographic column was prepared by dissolving 6.370 grams of diethylene glycol in a mixing solution of 20 ml. ethyl ether and 9 ml. chloroform³. 21.760 grams of 14-20 mesh, sieved, washed and dried particles of C-22 Firebrick was then poured into the glycol-ether-chloroform solution. The coated particles, after being well stirred, were dried under 30 mm. Hg vacuum on a water bath maintained at 30°C. Its total weight was checked every 30 minutes to prevent the coated particles from being overdried. Five hours later, the total weight reduced to the summation of the initial weight of diethylene glycol and Firebrick. This indicated that the ether and chloroform, which only serve as diluent for diethylene glycol, had been driven out. Because the vapor

¹. Fisher Scientific Company, Bedford, Ohio.

². Ainsworth Company, Denver, Colorado.

³. Ether-chloroform solution served as a diluent to assure a uniform coating of diethylene glycol on Firebrick. Pure ether was not used because it did not completely dissolve diethylene glycol. Both the ether and chloroform were Baker reagent grade.

pressure of ether and chloroform at 30°C are 540 mm. Hg and 230 mm. Hg, respectively, whereas that of diethylene glycol is only 0.015 mm. Hg, the loss of diethylene glycol during the drying process should have been negligible.

The coated Firebrick particles, stored until used in a calcium chloride filled desiccator to prevent the adsorption of water by diethylene glycol, was packed into a 3-foot copper tube of 1/4 inch O.D. and 3/16 inch I.D.; 7.996 grams of coated particles were packed into the column. The total weight of diethylene glycol inside the column was calculated to be 1.809 grams.

The 1,2,4 trichlorobenzene gas chromatographic column was prepared in the same manner. Pure ethyl ether instead of ether-chloroform solution was used as the diluent. The coated Firebrick was packed into a 1 meter, 1/4 inch O.D. glass tube. 5.7516 grams of coated particles was packed into the column and the 1,2,4 trichlorobenzene inside the column was calculated to be 1.6803 grams.

The prepared gas chromatographic column (T) was installed in an inverse U shape vertically inside the column oven (P) of a Perkin-Elmer Vapor Fractometer Model 154C. The temperature of the oven surrounding the column was maintained within $\pm 0.1^\circ\text{C}$ by a thermistor-controlled electric heater on the top of the oven. Hot air was circulated throughout the oven by a fan. Three thermocouples (O_3 , O_4 , O_5) were placed on the outer wall of the column, seven inches apart longitudinally from each other. The differences of the temperature indicated by the three thermocouples was less than 0.2°C . A fourth thermocouple had been inserted into the center of the column through a tee connection and a rubber serum cap. No

measurable difference (less than 0.05°C) of temperature had been detected between the thermocouple inside and that outside the wall at the corresponding elevation. Therefore, the fourth thermocouple was eliminated to avoid the possibility of leakage from the gas stream passing through the column. The temperature reading of the thermocouple (O_4) located in the middle of the three on the outside wall of the column, was taken as the temperature of the column. All the thermocouples were calibrated against an NBS certified mercury thermometer with $1/10$ degree centigrade subinterval. The fifty-six experimental points, covering the temperature range of 26°C to 92°C , were fitted by a fourth power orthogonal polynomial equation using a Burroughs 220 computer. The standard deviation of fitted curve values and experimental values is $\pm 0.07^{\circ}\text{C}$ (± 2 microvolts) with the maximum deviation of $\pm 0.15^{\circ}\text{C}$ (± 5 microvolts). The millivoltage output of the thermocouples was measured by a Leeds and Northrup Model #8662 Potentiometer with a precision of ± 3 microvolts.

To reduce the evaporation of the absorbing liquid (diethylene glycol or trichlorobenzene) in the column, a "pre-saturation" column (R) was installed in the column oven preceding the sample injection block (S) and chromatographic column (T) in the path of gas flow. The two-foot long, $3/16$ inch I.D. pre-saturation column was packed with 4 grams of diethylene glycol or trichlorobenzene coated coarse (greater than 14 mesh) Firebrick C-22 (weight ratio of diethylene glycol or trichlorobenzene to Firebrick is 75:100). The carrier gas stream was saturated, or nearly saturated, by the diethylene glycol or trichlorobenzene at the same temperature as the chromatographic column before entering the latter column; hence the vaporization of the diethylene glycol or trichlorobenzene in the latter column

should have been greatly suppressed.

The detector of the gas chromatograph is a thermistor type thermal conductivity cell. (Ionization detectors, both beta ray and flame type, are not suitable for the present experiment because the detectors become insensitive when the carrier gas contains more than trace amount of solute.) The temperature sensitive thermistors formed the four arms of a Wheatstone bridge. The difference in the concentration of the solute in the column inlet and outlet stream will cause an unbalance on the bridge circuit. The output signal is registered on a Leeds and Northrup millivolt recorder (0 to 5 millivolts range) which has a time constant of one second. The short time constant of the recorder, together with the small dead volume (0.1 millimeter) of the detector cell, assures a rapid response to the peak concentration.

The column inlet gauge pressure was measured by a diisodecyl phthalate filled manometer. It was found experimentally that the pressure drop from the measuring point to the true column inlet, and pressure drop from the column exit to the atmosphere were on the order of 0.1 mm. Hg, respectively, at the maximum flow rate (100 milliliter per minute) used in this study. Therefore, the pressures read from the manometer and a barometer, which was standardized against a precision barometer in the School of Chemical Engineering, Georgia Institute of Technology, calibrated to 0.05 mm. Hg by Edwards (43), were taken as the inlet and outlet column pressure.

CHAPTER V

EXPERIMENTAL PROCEDURES

At the beginning of a run, the whole system was checked for gas leakage. Helium gas was admitted into the gas chromatograph and both inlet and exit ends were blocked off when the pressure inside the chromatographic column had reached seven to eight inches of water. The rate of decrease of pressure, observing from the diisodecyl phthalate manometer (M), indicated the rate of leakage. No more leakage than two inches of water per hour, which roughly corresponding to two milliliters of gas per hour, or less than 0.1% of the flow rate of the carrier gas, was accepted. The saturators were then filled about three-fourths full with liquid solute (benzene or n-hexane). Water was added to the water bath (F) until the saturators and de-entrainment trap were completely covered. The water bath was heated or cooled to a pre-determined temperature. The heater of the Vapor Fractometer was turned on to maintain the column oven (P) at a constant temperature. The heating coil (N) wrapped along the gas flow path was also turned on to maintain the temperature of tube, as indicated by thermocouples (O_1), about 10°C above the temperature of the water bath. After these three temperatures had reached the desired levels, the valve of the helium tank (A) was opened to let helium bubble through the saturators and enter the column. The rotameter (D) gave a fairly accurate value of the flow rate which was controlled by the pressure regulator (B) and needle valve (E). (The flow rate was measured more precisely by the soap flow meter (X) at the exit.)

After the gas had been flushing through the chromatographic column (T) for at least half an hour, the Leeds and Northrup Millivoltage Recorder was turned on. A stable base line indicated that the equilibrium condition had been reached inside the column because the base line could be maintained at a constant level only when the concentration of solute in the column inlet stream was the same as that in the exit stream. It usually took from one-half to four hours, depending on the concentration of solute in the carrier gas and column temperature to reach this equilibrium condition.

The Turner adsorption bottle (U), which was purged by helium gas at 380°F for at least four to five hours, was weighed to 0.1 milligram. The room temperature, pressure and humidity during weighing were recorded. After the state of equilibrium had been reached inside the chromatographic column, the Turner adsorption bottle was connected to the exit end of the column. The period of adsorption was carefully timed. The flow rate of solute-free helium, coming out of the exit end of the Turner adsorption bottle, was measured by the soap film meter (X).

Samples of liquid solute in the range of 0.01 to 10.0 microliters, were injected, using Hamilton microsyringes¹, into the chromatographic column (T) through the sample injection block (S) where a small heater vaporized the sample immediately. The liquid samples were injected along with 1.0 to 5.0 microliters of air. An air peak and solute peak would

¹Manufactured by Hamilton Company, Witter, California. Two different models were used in the present study. Model 7001N is 1.0 microliter full capacity with 0.01 microliter subdivisions, and Model 701N is 10 microliter full capacity with 0.2 microliter subdivisions.

appear on the Recorder. The time interval between the appearances of the two peaks, timed by a Thompson electric stop timer, was recorded as the apparent retention time. Various sizes of samples were injected in random order to study the effect of samples size on the retention time. The minimum size of sample required to produce a visible peak depended on the column temperature and the concentration of the solute in the vapor phase. The higher the temperature the smaller the size of sample was required because the peak becomes sharper and hence easier to be identified. On the other hand, the higher of the concentration of the solute in the vapor phase the larger size of sample was required because of the increase of the base line noise. Except for a few runs operated at a column temperature below 70°C and vapor concentration greater than 30 mole per cent where a minimum sample size of 3 to 5 microliter was required to produce a visible peak, the smallest sample size used in every run was below 1.0 microliter. (The chromatograms of benzene samples, with the sizes varied from 0.2 to 10 microliters, were reproduced from the recorder chart and shown in Fig. 3.) The flow rates were measured before and after the injection of a sample. The column temperature, temperature inside the soap film flow meter, and reading of manometer and barometer were also recorded.

After four to ten samples had been injected and the adsorption time was over forty minutes, the Turner adsorption bottle (U) was closed and disconnected from the gas stream. It was weighed to 0.1 milligram. The difference in the weight of the adsorption bottle before and after the adsorption, corrected for the effect of changes in room temperature, pressure, and humidity on the weighing, if any, and the amount of solute injected, was the net amount of solute adsorbed from the carrier gas stream.

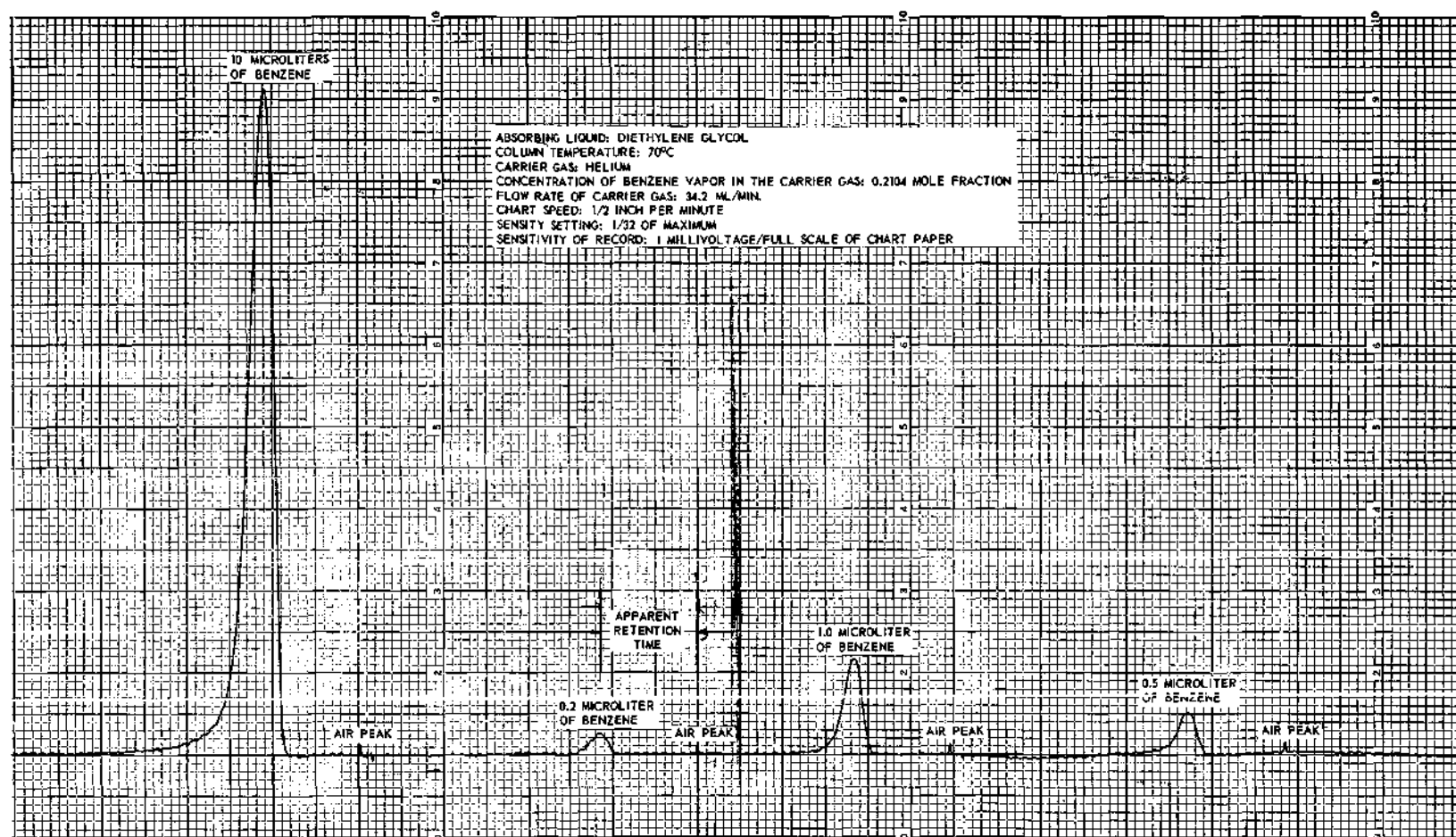


Figure 3. Chromatograms of Benzene Samples of Various Sizes.

The Turner adsorption bottle was heated to 380°F while purged by helium gas overnight to drive out the solute which had been adsorbed. The bottle was then ready for the next run.

A period of from three to five hours was required to make a set of measurements at a specific column temperature and vapor phase concentration.

CHAPTER VI

CALCULATION PROCEDURES, EXPERIMENTAL RESULTS
AND DISCUSSIONS

Calculation Procedures.--The procedures for calculation of the activity coefficient and the concentration of the solute in the liquid phase by GLC method are summarized in the following steps. A sample calculation is presented in Appendix IV.

- 1) Calculation of the mole fraction of solute in the gaseous mobile phase:

By combining equations (63), (64), (66), substituting 62,363 for R and $(273.16 + t_f)$ for T_f and re-arranging, one obtains,

$$y_2^o = \frac{62,363(W_2/M_2)(273.16 + t_f)Z_{1f}}{(\theta_D)(V_{fw}^i)(P_f - P_n) + 62,363(W_2/M_2)(273.16 + t_f)Z_{1f}} \quad (71)$$

where Z_{1f} is calculated from equation (65), W_2 , t_f , θ_D , V_{fw}^i , P_f , are experimental data, M_2 is the molecular weight of the solute, B_{11} is the second virial coefficient of helium, P_n , the vapor pressure of water at the temperature of flow meter, t_f , is taken from the Steam Tables by Keenan and Keys (44).

- 2) Calculation of $(N_m - \bar{G})$:

By substituting 62,363 for R and $(273.16 + t_f)$ for T_f , equation (70) becomes:

$$N_m - \bar{G} = (V'_{fw}) \left(\frac{1}{273.16 + t_f} \right) \left(\frac{1}{1 - y_2^o} \right) \left(\frac{P_f - P_n}{62,363 Z_{1f}} \right) (\theta_R) \quad (72)$$

where θ_R , t_1 as well as t_f , V'_{fw} , P_f are experimental data.

3) Calculation of the equilibrium constant, K_2 :

$$K_2 = \frac{1}{2}(2y_2^o + a) + \frac{1}{2} \left[(2y_2^o + a)^2 - 4(y_2^o)^2 \right]^{\frac{1}{2}} \quad (40)$$

where

$$a = \frac{(1 - y_2^o) W_s}{(N_m - \bar{G}) M_s f_p} \quad (41)$$

and f_p was calculated from equation (39).

4) Calculation of the correction factor for the imperfection of the vapor phase, ϕ :

$$\ln \phi = \ln \frac{Z_2^o}{Z_m} - 2(Z_2^o - 1) - \frac{V_{2L}}{RT} (P_m - P_2^o) + \frac{2P_m}{Z_m RT} (y_1 B_{12} + y_2 B_{22}) \quad (62)$$

where

$$y_2 = y_2^o \quad (73)$$

$$y_1 = 1 - y_2^o \quad (74)$$

$$P_m = 1/2(P_1 + P_o) \quad (75)$$

$$T = t_1 + 273.16 \text{ } ^\circ\text{K} \quad (76)$$

P_2^0 , the vapor pressure of solute was calculated from the following Antoine type equations given by the API Project 44 (38).

$$\text{Benzene:} \quad \log P_2^0 = 6.90565 - \frac{1211.033}{220.790 + t_1} \quad (77)$$

$$(P_2^0 = 40 \text{ to } 1500 \text{ mm. Hg})$$

$$\text{n-hexane:} \quad \log P_2^0 = 6.87776 - \frac{1171.53}{224.366 + t_1} \quad (78)$$

$$(P_2^0 = 10 \text{ to } 1500 \text{ mm. Hg})$$

Z_2^0 and Z_m were calculated from equations (61) and (60), respectively.

The value of V_{2L} was taken from the data given by API Project 44 (38).

The determination of B_{11} , B_{12} and B_{22} has been discussed in the section "Correction for the Imperfection of the Vapor Phase" of Chapter II.

5) Calculation of the activity coefficient of solute in the liquid phase:

$$\gamma_{2L} = \phi \frac{K_2 P_m}{P_2^0} \quad (45)$$

It was noticed that $(N_m - \bar{G})$, hence also K_2 and γ_{2L} calculated from it, is slightly affected by the size of solute sample injected. During each run, in general, four to ten samples of various sizes up to 10 microliters were injected. The activity coefficient, γ_{2L} , calculated from equation (45) was plotted against the volume of sample injected, s .

The extrapolated value of γ_{2L} at zero sample volume was taken as the true activity coefficient of the solute. The effect of the sample size will be discussed further in the next section of the chapter.

6) Calculation of the mole fraction of solute in the liquid phase:

The extrapolated value of γ_{2L} at zero sample size was substituted into the following equation which was obtained by re-arranging equation (44).

$$x_2^o = \frac{\phi y_2^o P_m}{\gamma_{2L} P_2^o} \quad (79)$$

Experimental Results.--The activity coefficients of benzene in the binary system of diethylene glycol and benzene were studied at the three different temperature levels. Twenty-three runs, with four to ten samples for each run, were carried out at the column temperature of 50°C. The concentrations of benzene in the vapor phase varied from run to run covering a range from zero to 30.0 mole per cent. The corresponding equilibrium concentrations of benzene in the liquid phase were zero to 31.1 mole per cent. Twenty runs were carried out at 70°C and twelve runs were carried out at 90°C. The concentrations of benzene in the vapor phase varied from zero to 55.6 mole per cent. They correspond to concentrations in the liquid phase from zero to 24.1 mole per cent at 70°C and zero to 9.08 mole per cent at 90°C, respectively. According to the experimental data of Johnson and Francis (45), diethylene glycol and benzene are completely miscible in the concentration ranges involved in this study, although they form two partial miscible phases at higher concentrations of benzene. (see Appendix V)

The activity coefficients of n-hexane in the second binary system of 1,2,4 trichlorobenzene and n-hexane were studied only at a temperature of 30°C. The concentrations of n-hexane in the vapor phase covered a

range from zero to 13.4 mole per cent; the corresponding equilibrium concentrations of benzene were zero to 39.8 mole per cent.

The experiments were actually carried out within $\pm 1.5^\circ\text{C}$ from the nominal temperatures. All the calculations were based on measured temperatures which had an accuracy of $\pm 0.2^\circ\text{C}$. Because it was found that the activity coefficient is not sensitive to a small change in temperature, the final calculated values were grouped into these four temperature levels. The total pressure inside the column varied slightly from run to run in the range of 735 to 753 mm. Hg. The results obtained were tabulated in Tables 1, 2, 3, and 4, respectively, for 50°C , 70°C , and 90°C , the three temperature levels of the system 1 and 30°C of system 2.

The run numbers in the first column of these tables are given in chronological order, whereas the experimental results are tabulated in order of increasing values of x_2 . The random sequence of measurements was designed to reduce any systematical experimental errors. One such possible error, for example, is the error due to the loss of absorbing liquid inside the column during the prolonged purge by the carrier gas; this will be discussed further in a subsequent section.

P_m in the second column is the total pressure inside the column, which is the average value of the inlet and outlet pressures of the column:

$$P_m = \frac{1}{2}(P_i + P_o) \quad (75)$$

the difference of P_i and P_o was maintained to be less than 20 mm. Hg throughout the present study. Therefore, the deviation of the average pressure from the pressure at every point in the column was less than

± 10 mm. Hg, which is less than $\pm 1.5\%$ of the total pressure.

The third column gives y_2^0 the mole per cent of the solute vapor in the mobile gaseous phase, calculated by equation (71), which will be discussed further in the subsequent section "Comparison of the concentration of the solute in the mobile gaseous phase measured by the adsorption method and that calculated from the vapor pressure of solute at the temperature of the saturator".

The fourth column is the correction for imperfection of the vapor phase as defined by the equation (43) and calculated from equation (62).

The fifth column is the activity coefficient of the solute in the liquid phase calculated by equation (45) and then extrapolated to the zero volume of sample size as described in the previous section "Calculation Procedures".

The sixth column is the mole per cent of solute in the liquid phase calculated from equation (79).

All the experimental data were measured with an accuracy of $\pm 1.5\%$ or better. (An analysis of the experimental accuracy of each measured quantities is presented in Appendix VI.) The overall accuracy in the measurement of the activity coefficient of the solute by the GLC method was thus estimated to be $\pm 3\%$. This estimation is partially confirmed by comparing the activity coefficients of Runs 1, 2, 5, 25, and 55 in Table 1, Runs 10, 11, and 38 in Table 2, Runs 43 and 44 in Table 3, and Runs 56 and 65 in Table 4. The reproducibilities of these runs in the several temperature levels were all better than $\pm 2\%$ from the average values. The agreement between y_2^0 and $(y_2^0)_s$ as listed in Tables 10, 11, 12, and 13 also indicates that the flow rate and y_2^0 have been adequately

measured with an accuracy of $\pm 3\%$. (The details of the comparison between y_2^0 and $(y_2^0)_s$ will be discussed in the subsequent section "Discussions of Experimental Results".)

Table 1

The Activity Coefficients of Benzene in Diethylene
Glycol at 50°C Measured by GLC Method

| Run No. | P_m mm. Hg | y_2^0 mole per cent | ϕ | γ_{2I} | x_2^0 mole per cent |
|------------|-----------------|--------------------------|--------|---------------|--------------------------|
| 1 | 742.6 | 0.0 | 1.016 | 6.79 | 0.0 |
| 2 | 752.9 | 0.0 | 1.016 | 6.72 | 0.0 |
| 5 | 742.0 | 0.0 | 1.016 | 6.69 | 0.0 |
| 25 | 749.6 | 0.0 | 1.016 | 6.64 | 0.0 |
| 55 | 749.7 | 0.0 | 1.016 | 6.65 | 0.0 |
| 9 | 744.2 | 4.33 | 1.012 | 6.25 | 1.91 |
| 24 | 743.9 | 4.89 | 1.012 | 5.97 | 2.24 |
| 23 | 744.9 | 6.27 | 1.011 | 5.84 | 2.94 |
| 8 | 745.5 | 6.32 | 1.010 | 5.92 | 3.01 |
| 4 | 740.3 | 7.91 | 1.009 | 5.73 | 3.78 |
| 22 | 743.6 | 7.79 | 1.009 | 5.60 | 3.82 |
| 21 | 743.8 | 9.47 | 1.008 | 5.34 | 4.94 |
| 7 | 745.9 | 10.24 | 1.007 | 5.18 | 5.49 |
| 3 | 743.6 | 11.53 | 1.001 | 5.18 | 6.16 |
| 20 | 740.4 | 12.37 | 1.006 | 5.05 | 6.76 |
| 6 | 743.0 | 12.42 | 1.005 | 5.04 | 6.89 |
| 30 | 745.4 | 14.37 | 1.004 | 4.69 | 8.44 |
| 19 | 739.4 | 14.49 | 1.004 | 4.66 | 8.53 |
| 27 | 747.2 | 18.01 | 1.001 | 4.31 | 11.56 |
| 28 | 746.0 | 21.84 | 0.999 | 3.78 | 15.87 |
| 26 | 743.2 | 24.10 | 0.997 | 3.54 | 18.24 |
| 29 | 747.4 | 27.88 | 0.994 | 3.02 | 25.27 |
| 40 | 747.5 | 30.04 | 0.993 | 2.61 | 31.08 |

Table 2

The Activity Coefficients of Benzene in Diethylene
Glycol at 70°C Measured by GLC Method

| Run No. | P_m mm. Hg | y_2^0 mole per cent | ϕ | z_2 | x_2^0 mole per cent |
|------------|-----------------|--------------------------|--------|-------|--------------------------|
| 10 | 743.0 | 0.0 | 1.028 | 6.49 | 0.0 |
| 11 | 745.9 | 0.0 | 1.028 | 6.40 | 0.0 |
| 38 | 741.4 | 0.0 | 1.027 | 6.51 | 0.0 |
| 12 | 746.8 | 5.07 | 1.024 | 6.35 | 1.10 |
| 13 | 746.5 | 6.44 | 1.023 | 6.19 | 1.45 |
| 14 | 745.6 | 8.12 | 1.022 | 6.09 | 1.86 |
| 15 | 745.3 | 8.99 | 1.021 | 6.02 | 2.07 |
| 16 | 745.7 | 10.38 | 1.020 | 5.84 | 2.48 |
| 17 | 746.1 | 12.26 | 1.019 | 5.56 | 3.07 |
| 18 | 745.6 | 14.64 | 1.018 | 5.55 | 3.63 |
| 31 | 745.5 | 19.00 | 1.016 | 5.35 | 4.64 |
| 33 | 743.9 | 21.04 | 1.015 | 5.18 | 5.20 |
| 32 | 742.6 | 24.72 | 1.013 | 5.13 | 6.15 |
| 53 | 743.4 | 23.34 | 1.012 | 5.04 | 6.32 |
| 39 | 741.6 | 27.41 | 1.012 | 4.90 | 7.10 |
| 35 | 744.3 | 30.89 | 1.010 | 4.57 | 8.46 |
| 36 | 745.1 | 34.30 | 1.007 | 4.35 | 10.53 |
| 39 | 747.8 | 44.06 | 1.001 | 3.77 | 16.20 |
| 40 | 744.6 | 52.35 | 0.998 | 3.20 | 22.85 |
| 41 | 742.7 | 55.56 | 0.997 | 3.13 | 24.06 |

Table 3

The Activity Coefficients of Benzene in Diethylene
Glycol at 90°C Measured by GLC Method

| Run No. | P_m mm. Hg | y_2^o mole per cent | ϕ | γ_{2L} | x_2^o mole per cent |
|------------|-----------------|--------------------------|--------|---------------|--------------------------|
| 43 | 748.4 | 0.0 | 1.044 | 6.41 | 0.0 |
| 44 | 736.5 | 0.0 | 1.044 | 6.37 | 0.0 |
| 51 | 744.7 | 16.78 | 1.035 | 5.70 | 2.26 |
| 45 | 736.9 | 29.70 | 1.028 | 5.37 | 4.16 |
| 50 | 744.1 | 31.64 | 1.027 | 5.41 | 4.46 |
| 46 | 743.0 | 33.50 | 1.027 | 5.27 | 4.73 |
| 52 | 737.4 | 34.38 | 1.027 | 5.26 | 4.82 |
| 47 | 743.9 | 40.50 | 1.024 | 5.01 | 5.96 |
| 54 | 736.4 | 44.60 | 1.022 | 5.01 | 6.62 |
| 49 | 742.0 | 46.15 | 1.022 | 4.82 | 7.05 |
| 48 | 746.1 | 54.10 | 1.019 | 4.68 | 8.54 |
| 42 | 743.6 | 55.56 | 1.019 | 4.51 | 9.08 |

Table 4

The Activity Coefficients of n-Hexane in 1,2,4
Trichlorobenzene at 30°C Measured by GLC Method

| Run No. | P_m mm. Hg | y_2^o mole per cent | ϕ | γ_{2I} | x_2^o mole per cent |
|------------|-----------------|--------------------------|--------|---------------|--------------------------|
| 56 | 737.7 | 0.0 | 1.020 | 2.82 | 0.0 |
| 65 | 750.2 | 0.0 | 1.020 | 2.82 | 0.0 |
| 64 | 743.0 | 2.88 | 1.014 | 2.36 | 5.19 |
| 62 | 740.5 | 3.40 | 1.014 | 2.31 | 5.79 |
| 63 | 737.5 | 4.83 | 1.012 | 2.11 | 9.01 |
| 57 | 745.3 | 6.10 | 1.010 | 1.93 | 12.67 |
| 59 | 742.2 | 7.99 | 1.007 | 1.76 | 18.62 |
| 58 | 745.2 | 9.28 | 1.005 | 1.573 | 23.50 |
| 60 | 743.5 | 10.66 | 1.003 | 1.477 | 29.09 |
| 61 | 750.6 | 13.40 | 1.000 | 1.327 | 39.80 |

Discussions of Experimental Results:

The activity coefficients of solute presented in Tables 1, 2, 3, and 4 were calculated from the experimental data based on the following assumptions:

- 1) The characteristics of the columns used in these measurements did not change during the course of experiment. Specifically, there was no loss of absorbing liquid during the prolonged purge by the carrier gas.
- 2) In the measurement of y_2^0 by the adsorption method, the adsorption of solute in the charcoal is complete and no condensation of solute vapor occurred in the gas flow path.
- 3) The activity coefficients calculated are independent of the flow rate of carrier gas which varied from run to run.
- 4) The size of the sample injected is infinitesimally small. (When a finite amount of sample -- greater than 0.1 microliter -- was used, the activity coefficient calculated, γ_{2L} , was plotted against the volume of sample size injected, s . The extrapolated value of γ_{2L} at zero sample volume was taken as the true activity coefficient of the solute.)

In this section, the validity of these assumptions will be discussed based on the analysis of the experimental data:

- 1) The loss of the absorbing liquid of the chromatographic columns due to vaporization:

Although the vapor pressure of diethylene glycol is remarkably low -- 1.2 mm. Hg at 90°C (46) -- compared with that of benzene, the possible loss of diethylene glycol from the gas chromatographic column during the

prolonged purge by the carrier gas stream was still a matter of concern. To suppress the vaporization of diethylene glycol, a pre-saturation column was installed in the column oven preceding the gas chromatographic column (see Chapter IV, "Experimental Equipment"). The carrier gas stream was saturated, or nearly saturated, by the diethylene glycol in the pre-saturation column at the same temperature as the gas chromatographic column before entering the latter column. In addition, the loss of diethylene glycol inside the gas chromatographic column was monitored by the measurement of the activity coefficient at infinite dilution at the different ages of the column. Because all the activity coefficients measured were based on the initial weight of the diethylene glycol packed into the column, γ_{2L} would show a proportional increase if any loss of diethylene glycol should occur. Five runs were made to measure the activity coefficient of benzene at infinite dilution at a column temperature of 50°C. One was carried out at the beginning of the installation of the column and one at the end of the present experiments, with three additional runs in between. The column had been operated for a total of, approximately, 180 hours with about 100 hours at 50°C, 50 hours at 70°C and 30 hours at 90°C covering an experimental period of about four months. The results of these five runs, shown in the first five lines of Table 1, agree with each other within the experimental error. This indicates that no substantial amount of diethylene glycol had been vaporized during the whole period and that the pre-saturation column was effective.

The vapor pressure of 1,2,4 trichlorobenzene is relatively high compared to diethylene glycol. However, the chromatographic column which employed the former liquid as the absorbing liquid was operated at a lower

temperature of 30°C. The vapor pressure of 1,2,4 trichlorobenzene at 30°C is 0.82 mm. Hg (14) which is about the same as the diethylene glycol at 90°C. The 1,2,4 trichlorobenzene column was also protected by a pre-saturation column. The column has been operated for a total of 80 hours. Two runs were made to measure the activity coefficient of n-hexane at infinite dilution at the beginning and the end of the whole series of experiments. The results of the two runs which are listed in the first two lines in Table 4 agree with each other very well. This indicates that the pre-saturation column was effective and that no substantial loss of the 1,2,4 trichlorobenzene inside the chromatographic column occurred during the 80-hour operation period.

- 2) Comparison of the concentration of the solute in the mobile gaseous phase measured by the adsorption method and that calculated from the vapor pressure of solute at the temperature of the saturator:

If the carrier helium stream is completely saturated by the solute when it leaves the last saturator, the mole fraction of solute in the mobile gaseous phase may be calculated by the following thermodynamic relation:

Assuming no helium dissolves in the liquid phase, the latter remains as a pure solute liquid at phase equilibrium.

$$(\bar{f}_{2V})_s = (f_{2L})_s \quad (80)$$

where $(\bar{f}_{2V})_s$ = partial fugacity of the solute in the vapor phase at the temperature and pressure inside the saturator t_s and P_s .

$(f_{2L})_s$ = fugacity of the pure liquid solute at P_s and t_s

A correction factor for the imperfection of the vapor phase evaluated at

P_s and t_s can be defined in the same way as that of equation (43).

$$\phi_s = \frac{(\bar{f}_{2V})_s (P_2^O)_s}{(y_2^O)_s P_s (f_{2L})_s} \quad (81)$$

Combining equations (80) and (81), we obtain

$$(y_2^O)_s = \frac{(P_2^O)_s}{P_s \phi_s} \quad (82)$$

where $(y_2^O)_s$ = mole fraction of the solute in the vapor phase at equilibrium condition inside the saturator

$(P_2^O)_s$ = vapor pressure of the solute at t_s , mm. Hg

P_s = pressure at the exit of the last saturator, mm. Hg

$(P_2^O)_s$ was calculated from equation (77) or equation (78) by substituting t_s for t_1 . ϕ_s might be calculated from equation (62) by evaluating every term at t_s and P_s instead of the column temperature and the column pressure, and substituting $(y_2^O)_s$ for y_2 and $1 - (y_2^O)_s$ for y_1 . A trial and error procedure was required to evaluate $(y_2^O)_s$.

The mole fraction of the solute in the mobile gaseous phase measured by the adsorption method, y_2^O , and that calculated from the vapor pressure of solute at the temperature of the saturator, $(y_2^O)_s$, would be the same only if the following conditions were fulfilled:

- a) The helium stream was completely saturated with the solute when it left the saturator.
- b) No condensation of solute vapor occurred in the gas flow path before entering and after leaving the column.

- c) An equilibrium state was maintained inside the column, hence the absorbing liquid inside could not absorb any more solute. Thus the concentration of solute vapor in the inlet stream was equal to the concentration in the exit stream.
- d) The adsorption of solute by the activated charcoal inside the adsorption bottle was complete. The helium stream which came out of the adsorption bottle was free of solute.
- e) The flow rate was accurately measured.

The deviations between y_2^o and $(y_2^o)_s$, expressed as $\left[(y_2^o)_s - y_2^o \right] / (y_2^o)_s$, as shown in Tables 10, 11, 12, and 13 in the Appendix II, in general are less than $\pm 3\%$. This agreement indicates that the above conditions had been fulfilled.

3) The effect of flow rate:

The retention volume which has been corrected for the effect of pressure drop across the column, and hence the activity coefficient calculated from the retention volume, is independent of the flow rate of the carrier gas passing through the column. This has been proven by Martin and Synge (24) and Porter et al. (10). It was re-confirmed in this study as shown by the data in the following Table 5.

Table 5

Independence of the Activity Coefficient Calculated
by the GLC Method to the Flow Rate of the Carrier Gas

| <u>Run No.</u> | <u>Column Temp. °C</u> | <u>Flow Rate, V'_{fw}, ml./sec.</u> | <u>% 2L</u> |
|----------------|------------------------|--|-------------|
| 1 | 50 | 0.641 | 6.79 |
| 2 | 50 | 1.772 | 6.72 |
| 5 | 50 | 0.834 | 6.69 |
| 25 | 50 | 1.270 | 6.64 |
| 55 | 50 | 0.781 | 6.65 |
| 10 | 70 | 1.710 | 6.49 |
| 11 | 70 | 0.725 | 6.40 |
| 38 | 70 | 0.581 | 6.51 |

4) The effect of the sample size:

The effect of sample size on the retention volume has been discussed by Glueckauf (47), Deemter, et al. (48), Keulemans (49), and Everett and Stoddart (21). No generally applicable correlation has been reached. In the derivation of the basic equation of gas chromatography the solute injected has been assumed to be infinitesimally small (see Chapter II, "Theory"). To fulfill these assumptions, the sample injected should be kept as small as possible. On the other hand, the sample should be large enough to produce a visible peak on the recorder.

The minimum size of sample which could be injected to produce a visible peak varied from 0.01 microliter to 5.0 microliter as concentration of solute in the vapor phase increased. This increased sample size was necessary because the base line noise increased with increase in concentration of solute in the vapor phase. At constant vapor phase concentration, the higher the column temperature the smaller the sample size necessary to produce a detectable peak. At a column temperature of 90°C, the minimum sample size used in every run was below 0.2 microliter, and at other temperatures was, in general, below 1.0 microliter, except for a few runs operated at a vapor concentration greater than 30 mole per cent where a minimum sample size of 3 to 5 microliter was required to produce a visible peak. Even in the latter case, the sample size used is much smaller than that used by Adlard, et al. (19), Everett and Stoddart (21), and Funk and Houghton (22). During each run, in general, five or six samples of various sizes up to 10 microliters were injected to study the effect of sample size on the activity coefficients calculated. When the activity coefficient of solute, γ_{2L} , was plotted against the volume of

sample injected, s , in most cases a straight line such as Curves III and IV shown in Fig. 4 was obtained. However, at the column temperature of 70°C, in a certain range of the concentration ($y_2^0 = 0.20$ to 0.35) of benzene, the γ_{2L} vs. s curve has the characteristics of Curve II shown in Fig. 4; the activity coefficient began to level off when the sample size used was larger than 1 or 2 microliters. These curves, straight line or not, were extrapolated to the zero sample volume. The activity coefficients shown in Tables 1, 2, 3, and 4 are all these extrapolated values, except in the runs where the minimum size of sample used was so small (less than 0.1 microliter) that no such extrapolation was necessary.

The dependence of "apparent activity coefficient"¹ on the sample size, expressed as $\Delta \gamma_{2L} / \Delta s$, the change of activity coefficient per microliter increase of sample size, is tabulated in Table 6 along with the column temperature, the partial pressure of solute in the vapor phase, and the mole fraction of solute in the liquid phase. $\Delta \gamma_{2L} / \Delta s$ was the slope of the straight line best fitting the experimental points. In the cases where the γ_{2L} vs. s could not be fitted by a straight line, the slope in the steep region of the curve (see Curve II of Fig. 4) between $s = 0$ to $s = 1.0$ was measured.

For the system of diethylene glycol-benzene, at column temperatures of 50°C and 70°C, $\Delta \gamma_{2L} / \Delta s$ is, in general, within the range of 0.02 to 0.05 per microliter. The smallest sample injected for each run, as men-

¹The term "apparent activity coefficient" is used here to designate the activity coefficients which are calculated from equations (40), (41), and (45) before being extrapolated to the zero sample size.

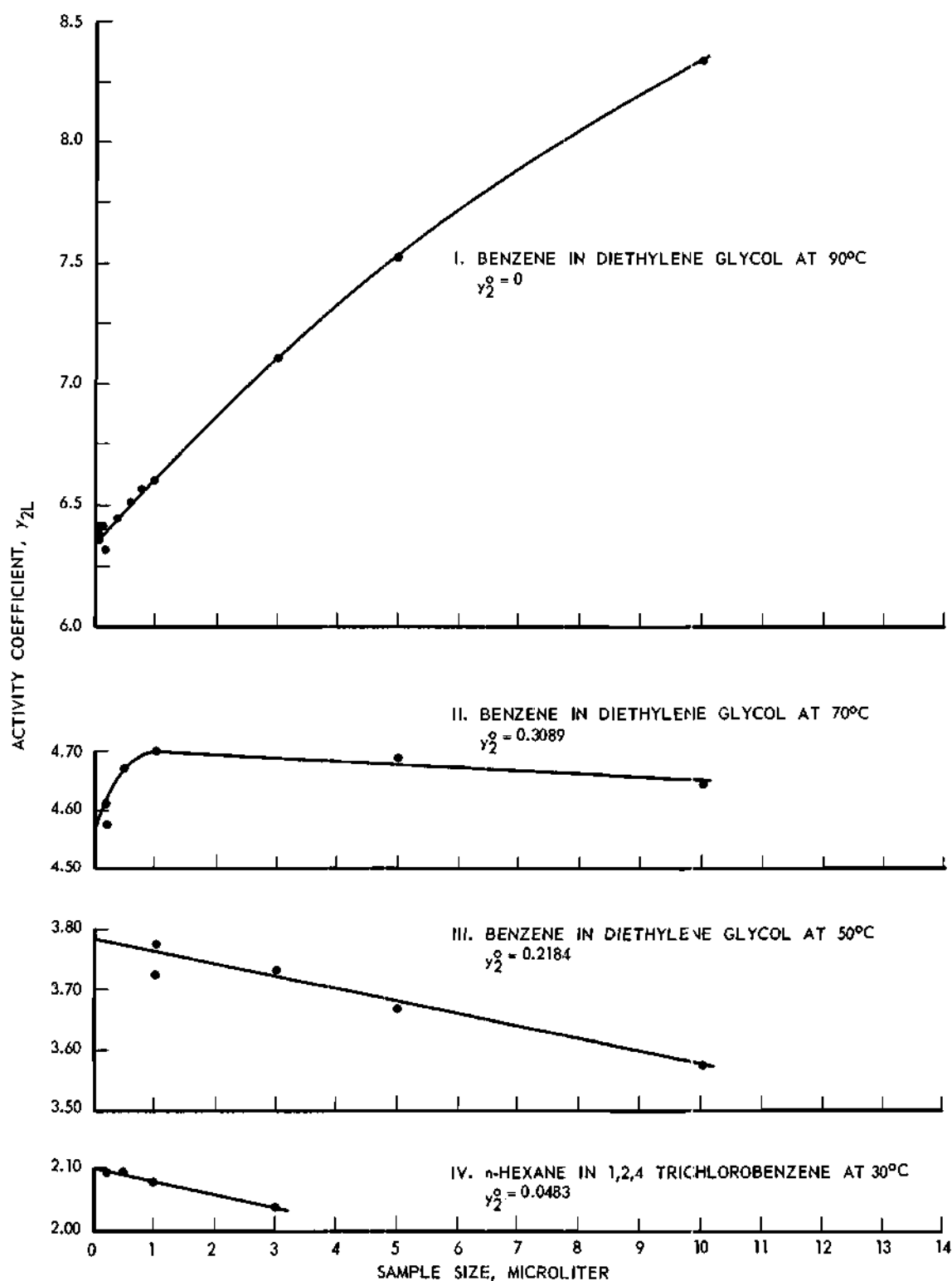


Figure 4. Effect of Sample Size on the Activity Coefficient.

Table 6

The Effect of Sample Size on the Activity Coefficients
of Benzene in Diethylene Glycol (System I) and of n-Hexane
in 1,2,4 Trichlorobenzene (System II)

| System | Column Temperature °C | x_2^0 | y_2^0 | K_2 | $K_2 + y_2^0$ | $\frac{\Delta y_2 / \Delta s}{(\text{microliter})^{-1}}$ |
|--------|-----------------------------|---------|---------|-------|---------------|--|
| I | 50 | 0.0000 | 0.0000 | 2.42 | 2.42 | * |
| I | 50 | 0.0191 | 0.0433 | 2.27 | 2.31 | * |
| I | 50 | 0.0301 | 0.0632 | 2.10 | 2.16 | * |
| I | 50 | 0.0549 | 0.1024 | 1.87 | 1.97 | * |
| I | 50 | 0.0844 | 0.1437 | 1.70 | 1.84 | - 0.03 |
| I | 50 | 0.1156 | 0.1801 | 1.56 | 1.74 | - 0.03 |
| I | 50 | 0.1576 | 0.2184 | 1.39 | 1.61 | - 0.02 |
| I | 50 | 0.1824 | 0.2410 | 1.32 | 1.56 | - 0.05 |
| I | 50 | 0.2527 | 0.2788 | 1.10 | 1.38 | - 0.02 |
| I | 70 | 0.0000 | 0.0000 | 4.60 | 4.60 | 0.09 |
| I | 70 | 0.0110 | 0.0507 | 4.61 | 4.66 | 0.05 |
| I | 70 | 0.0307 | 0.1225 | 3.99 | 4.11 | 0.04 |
| I | 70 | 0.0520 | 0.2104 | 4.05 | 4.26 | 0.14 |
| I | 70 | 0.0710 | 0.2741 | 3.86 | 4.13 | 0.12 |
| I | 70 | 0.1053 | 0.3430 | 3.26 | 3.60 | 0.03 |
| I | 70 | 0.1620 | 0.4406 | 2.72 | 3.16 | - 0.02 |
| I | 70 | 0.2285 | 0.5235 | 2.29 | 2.81 | - 0.01 |
| I | 70 | 0.2430 | 0.5560 | 2.31 | 2.87 | - 0.03 |

*. Activity coefficient is practically independent of the size of the samples injected.

Table 6 (continued)

| <u>System</u> | <u>Column Temperature °C</u> | <u>x_2^0</u> | <u>y_2^0</u> | <u>K_2</u> | <u>$K_2 + y_2^0$</u> | <u>$\frac{\Delta \gamma_{2L}}{\Delta s}$ (microliter)⁻¹</u> |
|---------------|--------------------------------------|---------------------------|---------------------------|-------------------------|---------------------------------|---|
| I | 90 | 0.0000 | 0.0000 | 8.28 | 8.28 | 0.28 |
| I | 90 | 0.0416 | 0.2970 | 7.14 | 7.44 | 0.27 |
| I | 90 | 0.0446 | 0.3160 | 7.09 | 7.41 | 0.19 |
| I | 90 | 0.0473 | 0.3350 | 7.08 | 7.41 | 0.17 |
| I | 90 | 0.0482 | 0.3438 | 7.13 | 7.47 | 0.32 |
| I | 90 | 0.0596 | 0.4050 | 6.80 | 7.20 | 0.27 |
| I | 90 | 0.0705 | 0.4615 | 6.55 | 7.00 | 0.29 |
| I | 90 | 0.0854 | 0.5410 | 6.33 | 6.87 | 0.27 |
| I | 90 | 0.0908 | 0.5560 | 6.12 | 6.67 | 0.19 |
| II | 30 | 0.0000 | 0.0000 | 0.903 | 0.903 | - 0.095 |
| II | 30 | 0.0519 | 0.0288 | 0.555 | 0.584 | - 0.035 |
| II | 30 | 0.0579 | 0.0340 | 0.587 | 0.612 | - 0.033 |
| II | 30 | 0.0901 | 0.0483 | 0.536 | 0.584 | - 0.021 |
| II | 30 | 0.1267 | 0.0610 | 0.481 | 0.542 | - 0.021 |
| II | 30 | 0.1862 | 0.0799 | 0.429 | 0.509 | - 0.022 |
| II | 30 | 0.2350 | 0.0928 | 0.395 | 0.483 | - 0.011 |
| II | 30 | 0.2909 | 0.1066 | 0.366 | 0.473 | - 0.007 |
| II | 30 | 0.3980 | 0.1340 | 0.337 | 0.471 | - 0.017 |

tioned before, was less than 1.0 microliter. Therefore, the uncertainty in the extrapolation of γ_{2L} to the zero volume of sample size is less than 1% of the activity coefficient calculated. At the column temperature of 90°C, $\Delta\gamma_{2L}/\Delta s$ increases to on the order of 0.2 to 0.3 per microliter; however, at this column temperature, the smallest sample injected was always less than 0.2 microliter, hence the uncertainty in the extrapolation of γ_{2L} to the zero volume of sample size is still no greater than 1% of the activity coefficient calculated. For the system of 1,2,4 trichlorobenzene -- n-hexane, $\Delta\gamma_{2L}/\Delta s$ is in the range of 0.007 to 0.03 per microliter except at the infinite dilution, $y_2^0 = 0$, $\Delta\gamma_{2L}/\Delta s = 0.09$. The uncertainty in the extrapolation for γ_{2L} at $y_2^0 > 0$ therefore is still in the order of 1 to 2% when the smallest sample injected for each run is less than 1.0 microliter. At infinite dilution, the smallest sample injected was 0.05 milliliter. Thus the uncertainty of extrapolation is also well below 1%.

Probably theoretically more significant than the absolute value of $\Delta\gamma_{2L}/\Delta s$ is its algebraic sign. The apparent activity coefficient was calculated based on the $(N_m - \bar{G})$ measured. The $(N_m - \bar{G})$ of a solute is a function of the concentration of solute in the vapor phase inside the column and hence the amount of the solute injected as may be shown by differentiating equation (37). All variables other than $(N_m - \bar{G})$ and y_2^0 are held constant.

$$\frac{\partial (N_m - \bar{G})}{\partial y_2^0} = \frac{K_2 W_s (K_2 - y_2^0) (2 - K_2 - y_2^0)}{M_s (K_2 - y_2^0)^3} \quad (83)$$

Because all the variables involved in equation (83) are positive in value,

and in the present study, K_2 is always greater than y_2^0 , the sign of $\frac{\partial (N_m - \bar{G})}{\partial y_2^0}$ will be determined by the term $(2 - K_2 - y_2^0)$,

$$K_2 + y_2^0 \begin{matrix} > \\ < \end{matrix} 2, \quad \frac{\partial (N_m - \bar{G})}{\partial y_2^0} \begin{matrix} < \\ > \end{matrix} 0 \quad (84)$$

y_2^0 has been defined as the concentration of the solute in the gas phase before the injection of a small sample. The injection of a relatively large sample may be considered as combined actions of first increasing the concentration y_2^0 , and then injecting a small sample. The increase of sample size, therefore, may be interpreted as the increase of y_2^0 . On the other hand, the increase of $(N_m - \bar{G})$ results in the decrease of apparent activity coefficient as can be seen from equations (40) and (41). If the $(N_m - \bar{G})$ and y_2^0 in equation (84) are replaced by γ_{2L} and s , respectively, then the "greater than" and "less than" signs must be reversed.

$$K_2 + y_2^0 \begin{matrix} > \\ < \end{matrix} 2, \quad \frac{\partial \gamma_{2L}}{\partial s} \begin{matrix} > \\ < \end{matrix} 0 \quad (85)$$

Table 6 shows a definite relation between the value of $(K_2 + y_2^0)$ and $\Delta \gamma_{2L} / \Delta s$. However, the latter seems to retain the negative sign until $(K_2 + y_2^0) = 3$ instead of changing sign at $(K_2 + y_2^0)$ equal 2 which is predicted by equation (85). This deviation may be attributed to a) the large sample increases the concentration of the solute inside the column, therefore decreases the value of K_2 which has been assumed to remain at constant in the differentiation; b) "the peak (retention) time increases because it takes longer for the center line of a larger slug to move to

the detector", as shown by Funk and Houghton (22). Both of these factors favor the negative sign of $\Delta \gamma_{2L} / \Delta s$.

CHAPTER VII

COMPARISON BETWEEN THE RESULTS OBTAINED BY THE GLC METHOD
AND THOSE OBTAINED BY THE STATIC EQUILIBRIUM METHOD

1) Diethylene glycol -- benzene system

The phase equilibrium of the binary system of diethylene glycol and benzene in the diethylene glycol rich region has been studied by Pierotti, et al. (13). The measurements were carried out at 50°C, 70°C, and 90°C by the static equilibrium method inside a 50 milliliter stirred vessel. Total pressures and concentrations of benzene in the liquid phase, obtained by measurement of refractive index, were reported. Activity coefficients of benzene were calculated by the present author from these data using the following equations:

$$\gamma_{2L} = \phi \frac{K_2 P_m}{P_2^0} = \phi \frac{\bar{P}_2}{x_2 P_2^0} \quad (45)$$

$$\text{where} \quad \bar{P}_2 = P_m - \gamma_{sL}(1 - x_2)P_d^0 \quad (86)$$

Because the data were measured in the diethylene glycol rich region, and P_d^0 , the vapor pressure of diethylene glycol, is small compared to the total pressure P_m , γ_{sL} , the activity coefficient of the diethylene glycol, might be assumed as 1.0 with negligible error in computing \bar{P}_2 . The correction factor for the imperfection of the vapor phase, ϕ , can be calculated from equation (62) by letting $y_1 = 0$, and $y_2 = 1.0$. Equation (62) then simplifies to

$$\ln \phi = \ln \frac{z_2^o}{z_m} - 2(z_m - z_2^o) - \frac{V_{2L}}{RT} (P_m - P_2^o) \quad (87)$$

The vapor pressure of benzene, P_2^o , used in equation (45) and equation (87) was based on equation (77). The value of V_{2L} was taken from the data given by API Project 44 (38). The calculated activity coefficients at the three temperatures, 50°C, 70°C, and 90°C are tabulated in Table 7 along with the total pressure and the mole fraction of benzene in the liquid phase.

The activity coefficients obtained by the static equilibrium method which were tabulated in Tables 1, 2, and 3, are plotted against the mole per cent of benzene in the liquid phase in Fig. 5, Fig. 6, and Fig. 7. The agreement between the two methods at dilute concentration range (x_2 less than 5 mole per cent) is within the overall experimental errors (± 3 per cent) of both sets of data at 50°C, 70°C, and 90°C. The values of γ_{2L} determined by the GLC method are seen to deviate from the data of Pierotti et al. (13) as the concentration of benzene increases. The maximum deviation is about 15 per cent. The deviation decreases with increasing column temperature. In all cases, the value of γ_{2L} obtained by GLC method is smaller than that obtained by Pierotti et al. (13).

2) 1,2,4 Trichlorobenzene -- n-Hexane System

The phase equilibrium of the binary system of 1,2,4 trichlorobenzene and n-hexane has been studied by Neckel and Kohlor (14) by the static equilibrium method. The total pressure of the binary solution covered a concentration range from $x_2 = 0$ to $x_2 = 1.0$ at 10°C, 20°C, and 30°C. Neckel and Kohler (14) calculated the activity coefficients of n-hexane

Table 7

The Activity Coefficients of Benzene in Diethylene Glycol
 Calculated from Equilibrium Data of Pierotti, *et al.* (13)

| Temp. °C | P_2^0 (mm. Hg) | P_m (mm. Hg) | \bar{P}_2 (mm. Hg) | x_2 mole per cent | $P_2/x_2 P_2^0$ | γ_{2L} |
|----------|---------------------|-------------------|-------------------------|------------------------|-----------------|---------------|
| 50 | 271.2 | 17.0 | 16.9 | 0.99 | 6.31 | 6.41 |
| 50 | 271.2 | 20.9 | 20.8 | 1.17 | 6.55 | 6.67 |
| 50 | 271.2 | 21.7 | 21.6 | 1.20 | 6.64 | 6.75 |
| 50 | 271.2 | 21.7 | 21.6 | 1.29 | 6.19 | 6.28 |
| 50 | 271.2 | 24.3 | 24.2 | 1.37 | 6.51 | 6.63 |
| 50 | 271.2 | 42.6 | 42.5 | 2.56 | 6.14 | 6.21 |
| 50 | 271.2 | 63.2 | 63.1 | 4.12 | 5.65 | 5.72 |
| 50 | 271.2 | 112.8 | 112.7 | 7.93 | 5.24 | 5.29 |
| 50 | 271.2 | 124.6 | 124.5 | 8.98 | 5.11 | 5.16 |
| 50 | 271.2 | 138.7 | 138.6 | 10.36 | 4.93 | 4.97 |
| 50 | 271.2 | 216.2 | 216.1 | 19.16 | 4.16 | 4.17 |
| 70 | 550.8 | 125.4 | 125.1 | 4.12 | 5.52 | 5.64 |
| 70 | 550.8 | 193.9 | 193.6 | 6.69 | 5.26 | 5.35 |
| 70 | 550.8 | 275.4 | 275.2 | 10.36 | 4.82 | 4.89 |
| 70 | 550.8 | 405.0 | 404.8 | 18.38 | 4.00 | 4.03 |
| 90 | 1021 | 72.5 | 71.6 | 1.17 | 5.98 | 6.23 |
| 90 | 1021 | 222.4 | 221.5 | 4.12 | 5.27 | 5.45 |
| 90 | 1021 | 344.8 | 343.9 | 6.69 | 5.04 | 5.19 |
| 90 | 1021 | 533.3 | 532.5 | 12.30 | 4.24 | 4.33 |
| 90 | 1021 | 723.6 | 722.8 | 18.55 | 3.82 | 3.87 |

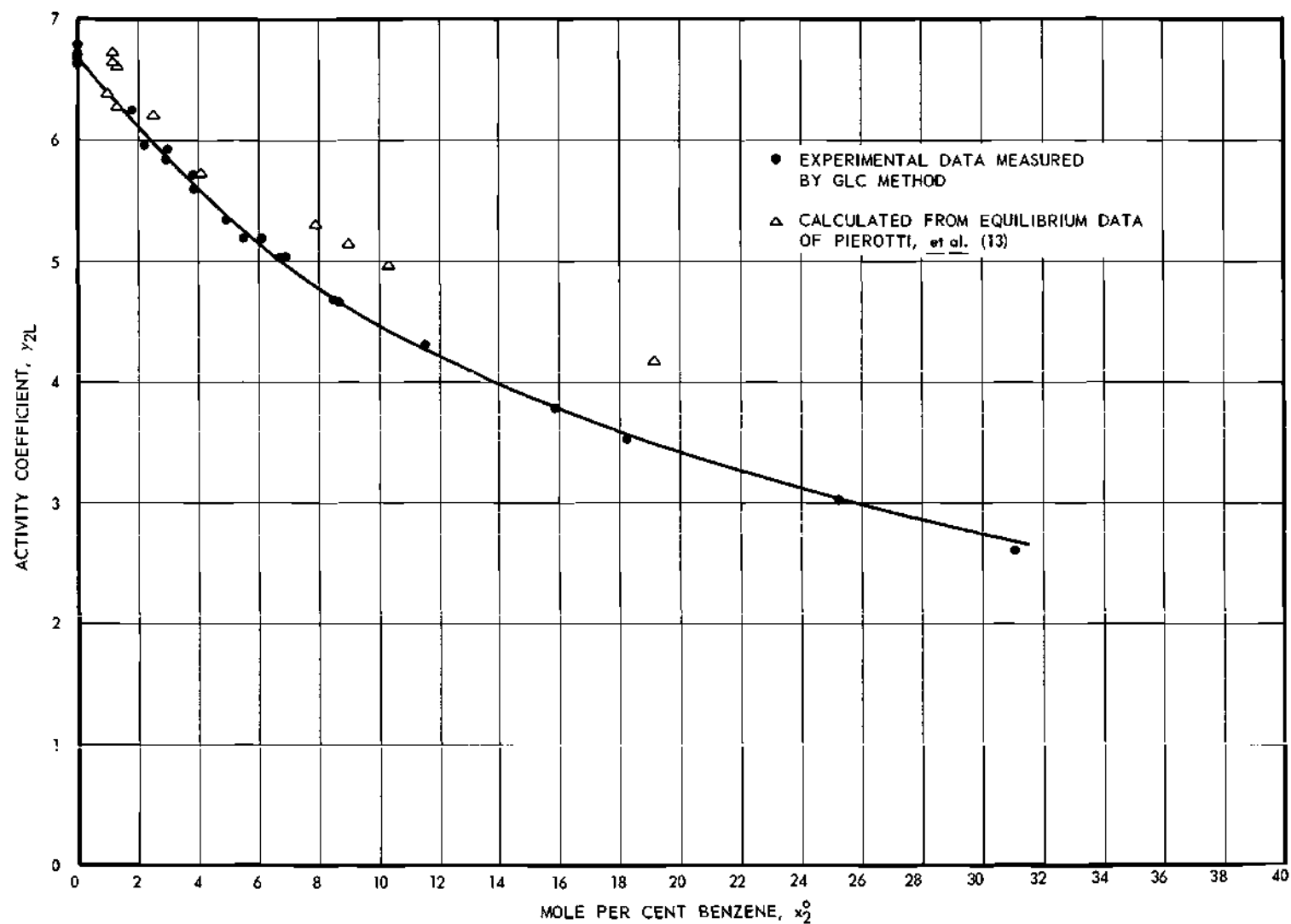


Figure 5. Activity Coefficient of Benzene Versus Its Mole Fraction in the Liquid Phase at 50°C in the System of Diethylene Glycol -- Benzene.

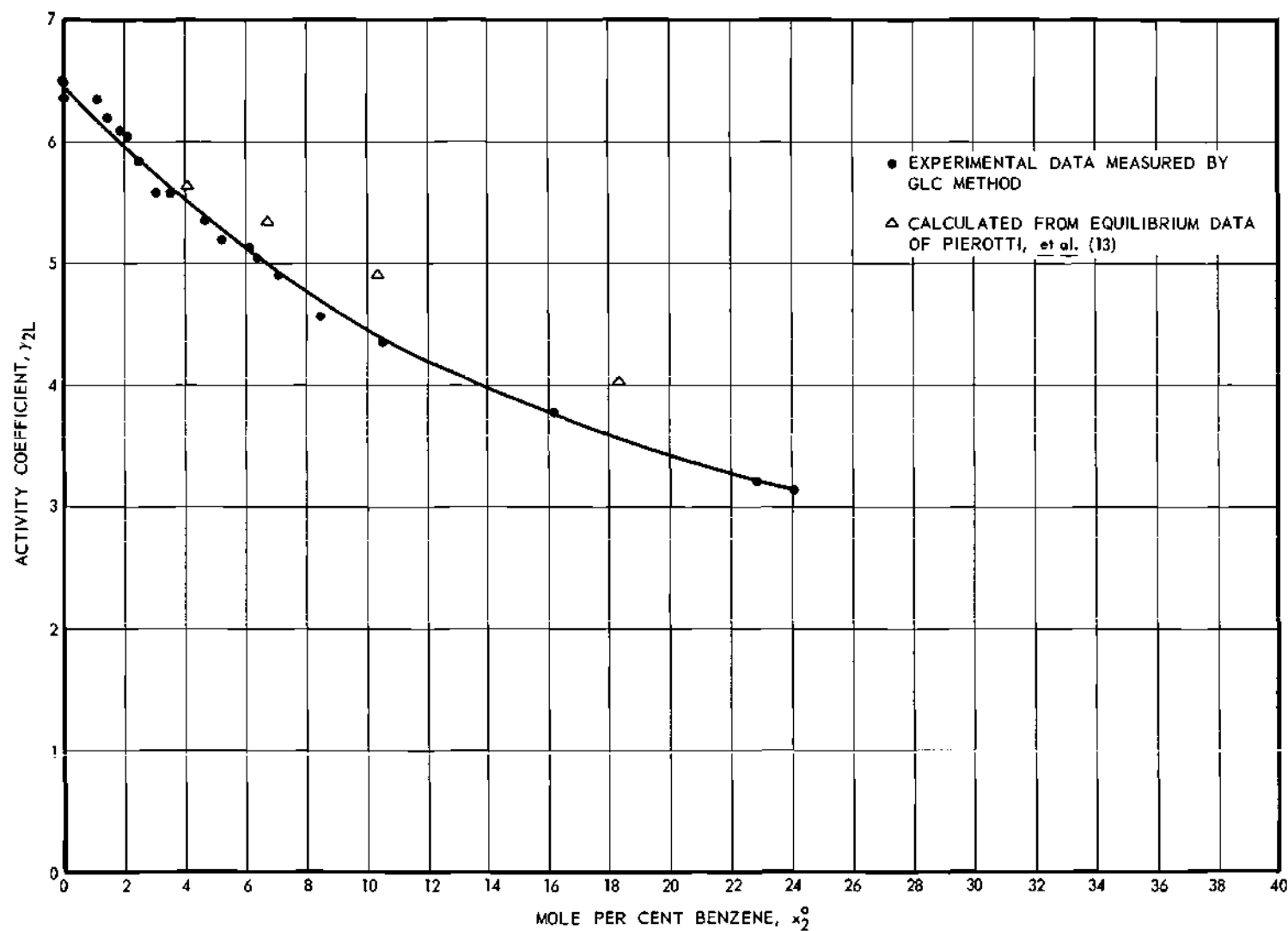


Figure 6. Activity Coefficient of Benzene Versus Its Mole Fraction in the Liquid Phase at 70°C in the System of Diethylene Glycol -- Benzene.

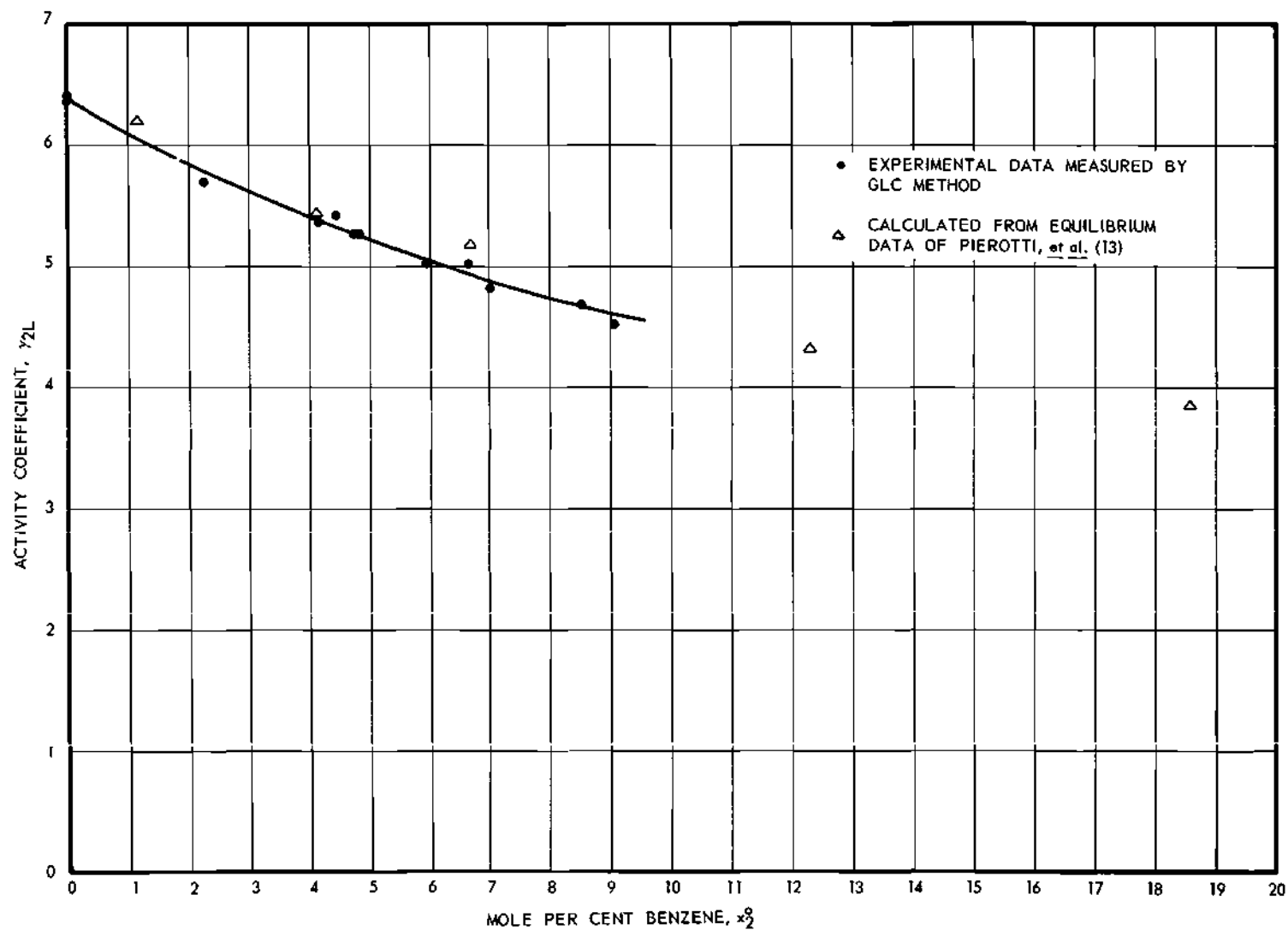


Figure 7. Activity Coefficient of Benzene Versus Its Mole Fraction in the Liquid Phase at 90°C in the System of Diethylene Glycol -- Benzene.

from their total pressure versus concentration data. The smoothed values at every tenth mole fraction of n-hexane in the liquid phase reported by them are reproduced in Table 8.

In the calculation of activity coefficients of n-hexane, Neckel and Kohler used the following equation to calculate the correction term for the imperfection of the gas phase:

$$\ln \phi = \frac{1}{RT} (V_{2L} - B_{22})(P_2^0 - P_m) \quad (88)$$

Equation (88) can be derived from the thermodynamic relation described by equation (57), however, a form of the second virial equation of state slightly different from equation (47) must be assumed:

$$\bar{V}_2 = \frac{N_2 RT}{P_2} + N_2 B_{22} \quad (89)$$

and the following mixing rule is employed:

$$B_{12} = \frac{1}{2} (B_{11} + B_{22}) \quad (90)$$

B_{22} of n-hexane used by Neckel and Kohler was calculated from van der Waals constants. It is - 820 ml./gm. mole at 30°C, compared to - 1800 ml./gm. mole calculated by Pitzer and Curl's (35) equation and the experimental data of - 1600 ml./gm. mole given by Lambert et al. (36) at the same temperature. Pitzer and Curl's equation was used to calculate B_{22} of n-hexane in the correction of the imperfection of the vapor phase for the data measured by the GLC method in the present study.

A comparison between the activity coefficients of n-hexane measured by GLC method and those by Neckel and Kohler can be made only if the two

Table 8

The Activity Coefficient of n-Hexane in 1,2,4 Trichlorobenzene
 Measured by Neckel and Kohler (14) by Static
 Equilibrium Method

| P_m mm. Hg | x_2 | $\log_{10} \gamma_{2L}$ | γ_{2L} |
|-----------------|-------|-------------------------|---------------|
| 6.08 | 0.01 | 0.45631 | 2.860 |
| 11.24 | 0.02 | 0.45205 | 2.832 |
| 16.27 | 0.03 | 0.44691 | 2.7985 |
| 21.16 | 0.04 | 0.44129 | 2.762 |
| 30.42 | 0.06 | 0.42792 | 2.679 |
| 38.68 | 0.08 | 0.40971 | 2.569 |
| 45.60 | 0.10 | 0.38556 | 2.430 |
| 51.72 | 0.12 | 0.36191 | 2.301 |
| 62.82 | 0.16 | 0.32242 | 2.101 |
| 72.26 | 0.20 | 0.28689 | 1.936 |
| 82.66 | 0.25 | 0.24885 | 1.774 |
| 91.91 | 0.30 | 0.21598 | 1.644 |
| 100.31 | 0.35 | 0.18721 | 1.539 |
| 107.98 | 0.40 | 0.16133 | 1.450 |

sets of data are calculated based on the same or equivalent equations for correcting the imperfection of the vapor phase. Because there is a difference between the correction equations used by Neckel and Kohler (14) and the present author, the activity coefficients of n-hexane reported by Neckel and Kohler (14) were re-calculated by the present author from the experimental data of total pressure versus concentration reported by them (14).

In the re-calculation, the same equations (45), (86), and (87) used to calculate γ_{2L} of benzene from Pierotti et al.'s data were used. The vapor pressure of 1,2,4 trichlorobenzene, P_d^0 , used in equation (86) is the experimental value reported by Neckel and Kohler (14) ($P_m = 0.82$ mm. Hg at $x_2 = 0.0$ in Table 9). The vapor pressure of n-hexane used in equation (45) was calculated from equation (78). The resultant value of 187.0 mm. Hg is slightly different from the experimental data of Neckel and Kohler ($P_m = 185.9$ mm. Hg at $x_2 = 1.00$ in Table 9). The value of V_{2L} , 132.5 ml./gm. mole, was taken from the data given by API Project 44 (38). The same value of V_{2L} was used by Neckel and Kohler in their computation.

The calculated activity coefficients of n-hexane in 1,2,4 trichlorobenzene at 30°C by the present author based on the experimental data of Neckel and Kohler were tabulated in Table 9 along with the original data of the total pressure and the mole fraction of n-hexane reported by Neckel and Kohler (14).

The three sets of data, a) activity coefficients of n-hexane measured by GLC method which were tabulated in Table 4, b) the same activity coefficients calculated from Neckel and Kohler's experimental data tabu-

Table 9

Activity Coefficients of n-Hexane in 1,2,4 Trichlorobenzene
at 30°C Calculated from Equilibrium Data of
Neckel and Kohler (14)

| P_m (mm. Hg) | \bar{P}_2 (mm. Hg) | x_2 mole fraction | $\bar{P}_2/x_2 P_2^0$ | γ_{2L} |
|-------------------|-------------------------|------------------------|-----------------------|---------------|
| 0.82 | 0.00 | 0.0000 | ---- | ---- |
| 8.85 | 8.04 | 0.0157 | 2.74 | 2.79 |
| 13.24 | 12.44 | 0.0245 | 2.71 | 2.76 |
| 15.68 | 14.88 | 0.0290 | 2.74 | 2.79 |
| 22.89 | 22.10 | 0.0440 | 2.69 | 2.73 |
| 26.16 | 25.38 | 0.0505 | 2.69 | 2.73 |
| 32.16 | 31.39 | 0.0640 | 2.62 | 2.66 |
| 33.55 | 32.78 | 0.0665 | 2.63 | 2.68 |
| 38.84 | 39.08 | 0.0850 | 2.46 | 2.50 |
| 46.50 | 45.77 | 0.1025 | 2.40 | 2.43 |
| 50.59 | 49.86 | 0.1170 | 2.28 | 2.31 |
| 63.84 | 63.15 | 0.1650 | 2.05 | 2.07 |
| 76.77 | 76.13 | 0.2230 | 1.82 | 1.85 |
| 97.00 | 96.44 | 0.3280 | 1.57 | 1.59 |
| 118.80 | 118.37 | 0.4770 | 1.33 | 1.34 |
| 125.70 | 125.31 | 0.5250 | 1.28 | 1.28 |
| 134.40 | 134.09 | 0.6240 | 1.15 | 1.15 |
| 162.00 | 161.87 | 0.8450 | 1.02 | 1.03 |
| 185.90 | 185.90 | 1.0000 | 1.00 | 1.00 |

lated in Table 9, and c) the smoothed values reported by Neckel and Kohler tabulated in Table 8, were plotted in Fig. 8 versus the mole per cent of n-hexane in the liquid phase. The activity coefficients calculated from Neckel and Kohler's data by the present author and the smoothed values reported by Neckel and Kohler are seen to agree with each other within the experimental error, $\pm 1.5\%$, reported by Neckel and Kohler (14). This results from the fact that the correction term for the imperfection of the vapor phase is a minor correction in the present case. Therefore, essentially identical values result even if two different correction terms have been employed.

The activity coefficients measured by GLC method and those calculated from the equilibrium data of Neckel and Kohler agree within the experimental errors of both sets of data (3%) at infinite dilution. The deviation increases to 7% as x_2 increases to 3% and reaches the maximum of 15% at $x_2 = 10\%$, and then decreases to 12 to 13% at higher concentrations. As in the system diethylene glycol -- benzene, the activity coefficients measured by the GLC method yield a lower value than those measured by the static equilibrium method.

The exact reason for the deviation which occurs in the higher concentration region of both systems is uncertain. It may be caused in part by the uneven distribution of the solute in the liquid phase inside the gas chromatographic column. The aggregation of the solute at the surface will increase the "effective concentration" of the solute in the liquid phase, and consequently yields a lower value of activity coefficient than it would have if the solute were uniformly distributed.

According to Funk and Houghton (22), who have studied the mechanism

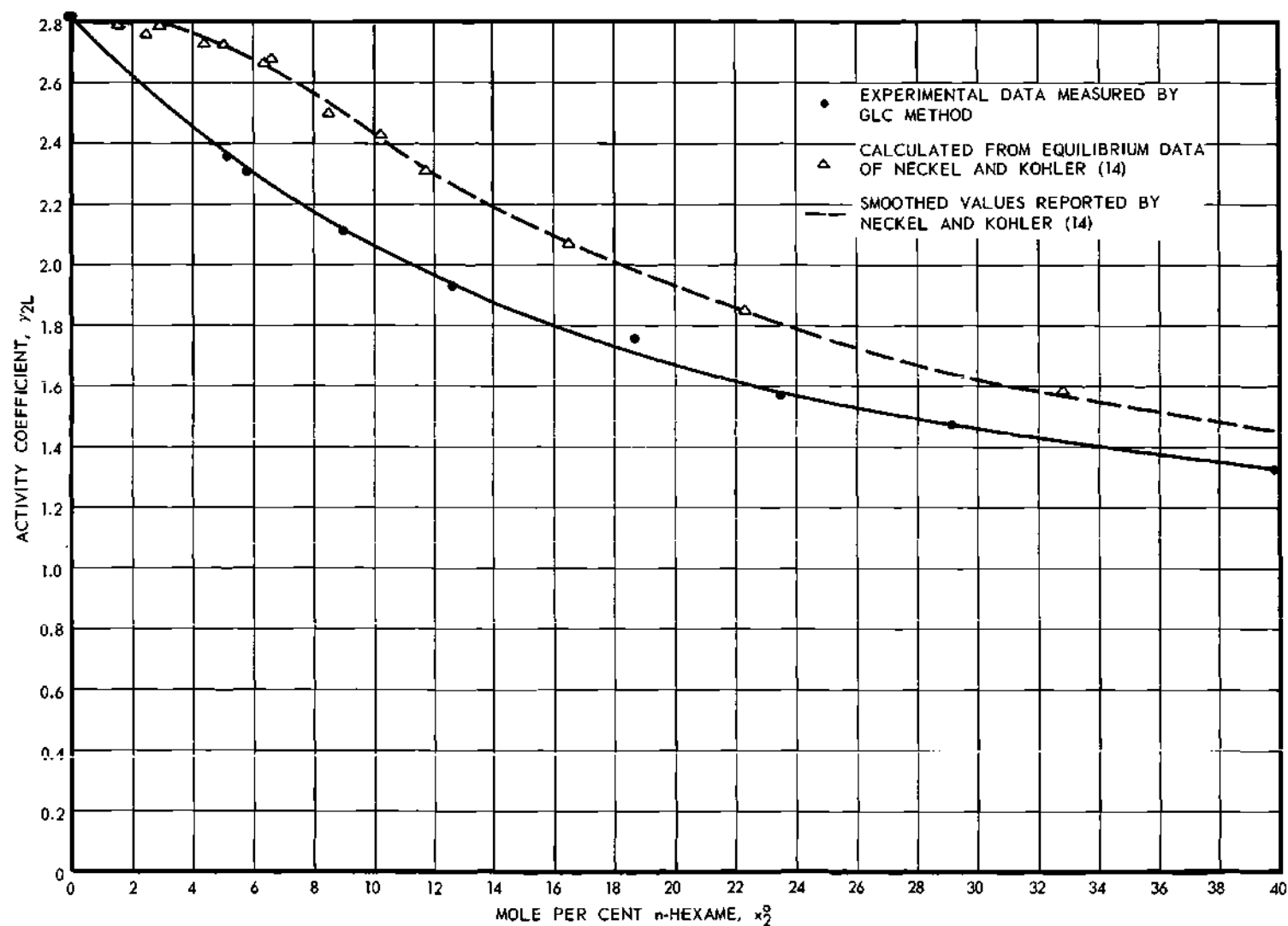


Figure 8. Activity Coefficient of n-Hexane Versus Its Mole Fraction in the Liquid Phase at 30°C in the System of 1,2,4 Trichlorobenzene -- n-Hexane.

of gas-liquid chromatography based on a "Lumped-Film Model", the effect of the finite mass transfer rate on the retention time is related to the vapor-liquid equilibrium constant, K , and molecular diffusivity in liquid phase, D_L . The greater the K and D_L , the greater the rate of mass transfer rate, and thus the more uniform the distribution of the solute in the liquid phase. This agrees with the experimental results of the present study that the higher the column temperature (the greater the K and D_L) the less the deviation between the activity coefficients measured by the GLC method and the static equilibrium method.

No check of the thermodynamic consistency can be made because the activity coefficients of only one component in the binary systems has been measured. Therefore, unless phase equilibrium data for the same systems are available from a third independent source, it is difficult to ascertain what portion of the deviation may be interpreted as the experimental error of the GLC method.

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

An equation has been derived, based on a theoretical plate model, to describe the concentration profile of a small volatile solute sample which is carried through a gas chromatographic column by a carrier gas which is insoluble in the column liquid. The column is packed with an inert solid which is coated with a non-volatile absorbing liquid. The equation of the concentration profile permits determination of the activity coefficient of the solute dissolved in the absorbing liquid by measuring the time required for its peak concentration to pass through the column.

Based on the experimental results obtained from the study of the two binary systems: diethylene glycol -- benzene and 1,2,4 trichlorobenzene -- n-hexane, the following conclusions may be drawn:

- 1) The activity coefficients of the solute (benzene or n-hexane) measured by the Gas-Liquid Chromatographic method (GLC) agree well with those obtained by the static equilibrium methods in the dilute concentration region where other methods are difficult to carry out. At infinite dilution the agreement appears to be within the experimental errors of the two methods.
- 2) In the region of higher concentration (concentration of solute in the liquid phase greater than 5 mole per cent) activity coefficients obtained by the GLC method agree less well with those obtained by the static equilibrium method, the deviation ranges from

3 per cent to a maximum of 15 per cent. In all instances the activity coefficients determined by the GLC method were lower. In the system of diethylene glycol -- benzene where the activity coefficients of benzene at the three different temperature levels, 50°C, 70°C, 90°C, have been studied, the deviation between the results obtained by the GLC method and the static equilibrium method is found to decrease with the increase of column temperature.

In addition to the above conclusions, the following associated results were observed:

- 1) By using a pre-saturation column preceding the gas chromatographic column, it was found that the characteristics of the gas chromatographic column did not change during the experiment period after a prolonged purge by the carrier gas. (180 hours for diethylene glycol column and 80 hours for 1,2,4 trichlorobenzene column.) This suggests that there was no appreciable loss of absorbing liquid inside the gas chromatographic column during the period.
- 2) Based on both the analytical analysis and the experimental results, the relation between the retention time and the solute sample size is found to be closely related to the equilibrium constant, K_2 , and the mole fraction of the solute in the vapor phase, y_2 .

Whereas the GLC method by no means can replace all the conventional static equilibrium methods in the vapor-liquid equilibrium study, it offers certain advantages in the measurement of the activity coefficient of a dilute solute in a relatively non-volatile solvent. No analysis of the composition of the liquid phase is required and hence the measurement maintains the same accuracy at dilute concentration. On the other hand,

the GLC method at present is seriously limited by the upper limits of concentration and temperature range it is able to cover.

Future study should be conducted in the high concentration region where a discrepancy between the results of GLC method and the static equilibrium methods was observed in the present study. Higher total pressure may be employed to increase the partial pressure of solute without the necessity of increasing the concentration of solute in the vapor phase. By this method the equilibrium concentration of the solute in the liquid phase may be considerably extended.

By using a pre-saturation column as employed in the present study or by other better means, the GLC method may possibly tolerate a vapor pressure of the absorbing liquid up to several millimeters of mercury. Investigations should be conducted to establish the upper limit because it is directly related to the temperature limit allowed by GLC method.

Further study may also be made in the application of GLC method in the vapor-liquid equilibrium of multicomponent systems which contain at least one relatively non-volatile component. The non-volatile component should be used as the absorbing liquid and the mobile gaseous phase should be composed of an inert carrier gas and the remaining volatile components. Retention time of every volatile component present would be measured in order to solve simultaneously the equations which relate the retention time and equilibrium constants of all the volatile components in a rather complicated form.

A P P E N D I C E S

APPENDIX I

INTEGRATION OF EQUATION (20)

$$\frac{dY_p}{dv} = Y_{p-1} - Y_p \quad (20)$$

Equation (20) may be solved vessel by vessel. Start with the first vessel, $p = 0$. The concentration of the solute of the inlet flow for the first vessel is always equal to y^0 , therefore, $Y_{p-1} = 0$. Equation (20) becomes:

$$\frac{dY_0}{dv} = -Y_0 \quad (91)$$

The solution of equation (91) with the initial condition, at $v = 0$, $Y_0 = Y_s$ is:

$$Y_0 = Y_s e^{-v} \quad (92)$$

The second vessel, $p = 1$, is considered next. By substituting $p = 1$ into equation (20), one obtains

$$\frac{dY_1}{dv} = Y_0 - Y_1 \quad (93)$$

Equation (92) and equation (93) are combined to obtain

$$\frac{dY_1}{dv} = Y_s e^{-v} - Y_1 \quad (94)$$

Equation (94) is a first order linear differential equation. Its solution is:

$$Y_1 = Y_s v e^{-v} + C_1' e^{-v} \quad (95)$$

The given initial condition is : at $v = 0$, $Y_1 = 0$, therefore $C_1' = 0$, then

$$Y_1 = Y_s v e^{-v} \quad (96)$$

For the third vessel, $p = 2$, equation (20) becomes:

$$\frac{dY_2}{dv} = Y_1 - Y_2 \quad (97)$$

Solving equation (97) in the same manner as solving equation (93), one obtains

$$Y_2 = Y_s \left(\frac{v^2}{2} \right) e^{-v} \quad (98)$$

For vessel p , it can be easily shown that:

$$Y_p = Y_s \left(\frac{e^{-v} v^p}{p!} \right) \quad (21)$$

APPENDIX II

COMPARISON OF THE CONCENTRATIONS OF THE SOLUTE IN THE MOBILE
GASEOUS PHASE MEASURED BY THE ADSORPTION METHOD AND THOSE CALCULATED
FROM THE VAPOR PRESSURE OF SOLUTE AT THE TEMPERATURE OF THE SATURATOR

The numerical values of y_2^o and $(y_2^o)_s$ of each experimental run, calculated by equation (71) and equation (82), are listed in Tables 10, 11, 12, and 13. The run numbers in the first column of these tables are listed in the same order as those listed in Tables 1, 2, 3, and 4 in Chapter IV to facilitate cross-reference. The last column of those tables listed the deviation between $(y_2^o)_s$ and y_2^o , which is defined as

$$\text{dev.} = \frac{(y_2^o)_s - y_2^o}{(y_2^o)_s} \quad (99)$$

Table 10

The Comparison of y_2^o and $(y_2^o)_s$ of Benzene
at Column Temperature of 50°C

| <u>Run No.</u> | y_2^o <u>mole per cent</u> | $(y_2^o)_s$ <u>mole per cent</u> | <u>dev.</u> |
|----------------|---------------------------------|-------------------------------------|-------------|
| 1 | 0.0 | 0.0 | --- |
| 2 | 0.0 | 0.0 | --- |
| 5 | 0.0 | 0.0 | --- |
| 25 | 0.0 | 0.0 | --- |
| 55 | 0.0 | 0.0 | --- |
| 9 | 4.33 | 4.95 | 0.127 |
| 24 | 4.89 | 5.08 | 0.037 |
| 23 | 6.27 | 6.39 | 0.019 |
| 8 | 6.32 | 6.49 | 0.026 |
| 4 | 7.91 | 8.05 | 0.017 |
| 22 | 7.79 | 7.97 | 0.023 |
| 21 | 9.47 | 9.70 | 0.024 |
| 7 | 10.24 | 10.15 | - 0.009 |
| 3 | 11.53 | 12.50 | 0.078 |
| 20 | 12.37 | 12.51 | 0.011 |
| 6 | 12.42 | 12.47 | 0.004 |
| 30 | 14.37 | 14.87 | 0.034 |
| 19 | 14.49 | 14.70 | 0.014 |
| 27 | 18.01 | 17.94 | - 0.008 |
| 28 | 21.84 | 22.22 | 0.017 |
| 26 | 24.10 | 24.63 | 0.022 |
| 29 | 27.88 | 27.45 | - 0.015 |
| 40 | 30.04 | 30.06 | 0.001 |

Table 11

The Comparison of y_2^C and $(y_2^C)_s$ of Benzene
at Column Temperature of 70°C

| <u>Run No.</u> | y_2^C <u>mole per cent</u> | $(y_2^C)_s$ <u>mole per cent</u> | <u>dev.</u> |
|----------------|---------------------------------|-------------------------------------|-------------|
| 10 | 0.0 | 0.0 | ----- |
| 11 | 0.0 | 0.0 | ----- |
| 38 | 0.0 | 0.0 | ----- |
| 12 | 5.07 | 4.94 | - 0.027 |
| 13 | 6.44 | 6.44 | 0.000 |
| 14 | 8.12 | 8.04 | - 0.010 |
| 15 | 8.99 | 8.97 | - 0.002 |
| 16 | 10.38 | 10.45 | 0.006 |
| 17 | 12.26 | 12.17 | - 0.007 |
| 18 | 14.64 | 14.46 | - 0.012 |
| 31 | 19.00 | 19.17 | 0.009 |
| 33 | 21.04 | 21.70 | 0.030 |
| 32 | 24.72 | 26.24 | 0.058 |
| 53 | 23.34 | 24.60 | 0.051 |
| 39 | 27.41 | 28.38 | 0.034 |
| 35 | 30.89 | 31.67 | 0.025 |
| 36 | 34.30 | 35.36 | 0.027 |
| 39 | 44.06 | 45.21 | 0.025 |
| 40 | 52.35 | 53.06 | 0.013 |
| 41 | 55.56 | 56.16 | 0.010 |

Table 12

The Comparison of y_2^c and $(y_2^c)_s$ of Benzene
at Column Temperature of 90°C

| <u>Run No.</u> | <u>y_2^c mole per cent</u> | <u>$(y_2^c)_s$ mole per cent</u> | <u>dev.</u> |
|----------------|---|---|-------------|
| 43 | 0.0 | 0.0 | ----- |
| 44 | 0.0 | 0.0 | ----- |
| 51 | 16.76 | 15.47 | - 0.083 |
| 45 | 29.70 | 29.85 | 0.005 |
| 50 | 31.65 | 33.83 | 0.064 |
| 46 | 33.50 | 34.26 | 0.022 |
| 52 | 34.38 | 34.06 | - 0.009 |
| 47 | 40.50 | 41.12 | 0.015 |
| 54 | 44.60 | 46.90 | 0.049 |
| 49 | 46.15 | 47.71 | 0.033 |
| 48 | 54.10 | 54.61 | 0.009 |
| 42 | 55.60 | 56.33 | 0.013 |

Table 13

The Comparison of y_2^c and $(y_2^o)_s$ of n-Hexane
at Column Temperature of 30°C

| <u>Run No.</u> | y_2^c <u>mole per cent</u> | $(y_2^o)_s$ <u>mole per cent</u> | <u>dev.</u> |
|----------------|---------------------------------|-------------------------------------|-------------|
| 56 | 0.0 | 0.0 | ----- |
| 65 | 0.0 | 0.0 | ----- |
| 64 | 2.88 | 2.84 | - 0.014 |
| 62 | 3.40 | 3.70 | 0.081 |
| 63 | 4.83 | 4.96 | 0.014 |
| 57 | 6.10 | 6.37 | 0.042 |
| 59 | 7.99 | 8.16 | 0.020 |
| 58 | 9.28 | 10.01 | 0.073 |
| 60 | 10.66 | 10.95 | 0.026 |
| 61 | 13.40 | 13.50 | 0.007 |

APPENDIX III

THE SECOND VIRIAL COEFFICIENTS
OF THE MIXTURE OF HELIUM AND BENZENE

In the absence of experimental P-V-T-y data, the second virial coefficient of a mixture must be estimated from the properties of its constituents. The second virial coefficient of a binary mixture, as derived from statistical mechanics, has been given as a quadratic function of the mole fraction in equation (49):

$$B_m = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \quad (49)$$

where B_{11} and B_{22} are the second virial coefficients of helium and benzene, respectively, as defined by equations (46) and (47) and B_{12} is an interaction coefficient.

Many different types of mixture rules have been suggested to estimate B_{12} from B_{11} and B_{22} . The most simple one consists in taking the arithmetic mean of these two:

$$B_{12} = \frac{1}{2} (B_{11} + B_{22}) \quad (100)$$

Adlard, et al. (19) used equation (100) to correct for imperfection of gas phase in their calculations of the activity coefficient of benzene at infinite dilution by GLC method. This arithmetical mean method has been pointed out by Guggenheim and McClashan (33) as having "no basis in theory, nor in experiment". It only gives an adequate answer when

$B_{11} = B_{22}$ and this is certainly not the case for helium and benzene.

A Lorentz-Berthelot mixture rule (32) was used by Techo (31) in the determination of the activity coefficients of non-polar ternary hydrocarbon systems. To use this mixture rule, the second virial coefficients of pure substances and mixtures must be expressed in a Berthelot type equation:

$$B = C - A/T \quad (101)$$

The mixture rules are:

$$C_{12} = \frac{(C_{11}^{1/3} + C_{22}^{1/3})^3}{8} \quad (102)$$

$$A_{12} = \sqrt{A_{11}A_{22}} \quad (103)$$

Techo (31) shows that B_{12} of the mixture of cyclohexane and benzene calculated from the mixture rule of Lorentz-Berthelot agrees well with the experimental data of Waelbroeck (50).

Guggenheim and McGlashan (33), based on the principle of corresponding states, found that the second virial coefficients of many pure substances can be described by a single universal function:

$$\frac{B}{V^*} = F\left(\frac{T}{T^*}\right) \quad (104)$$

For all gases, except hydrogen and helium, V^* and T^* may be taken as the critical volume and critical temperature of the gas. In the cases of helium and hydrogen pseudo-critical temperatures and pseudo-critical pressures are determined by fitting the available experimental values of

the second virial coefficient into equation (104). The following values for helium are given by Guggenheim and McGlashan (33).

$$V^* = 33.7 \text{ cm.}^3/\text{mole}$$

$$T^* = 7.66^\circ\text{K}$$

Guggenheim and McGlashan (33) have also proposed that equation (87) is applicable to a mixture; the equation having the form

$$\frac{B_{12}}{V_{12}^*} = F\left(\frac{T}{T_{12}^*}\right) \quad (105)$$

The mixture rules they suggested are:

$$(V_{12}^*)^{1/3} = \frac{1}{2} (V_{11}^*)^{1/3} + \frac{1}{2} (V_{22}^*)^{1/3} \quad (106)$$

$$T_{12}^* = (T_{11}^* T_{22}^*)^{1/2} \quad (107)$$

Guggenheim and McGlashan (33) show that B_{12} calculated from equations (105), (106), and (107) agrees well with the experimental values in the mixture of helium and argon. Everett and Stoddart (21) used this method to correct the imperfection of vapor phase in their calculation of the activity coefficient at infinite dilution by GLC method.

Prausnitz and Gunn (34) have pointed out that Guggenheim and McGlashan's method gives good results for mixtures of light components but gives progressively worse results as the sizes of the gas molecules increase. They introduce a third parameter which was developed previously by Pitzer and Curl (35) for the correction of the imperfection of

the pure gas:

$$\begin{aligned}
 B_{12} Z_{12}^* / V_{12}^* = & (0.1445 + 0.073 w_{12}) - (0.330 - 0.46 w_{12})(T_{r12})^{-1} \\
 & - (0.1385 + 0.50 w_{12})(T_{r12})^{-2} - (0.012 + 0.97 w_{12})(T_{r12})^{-3} \\
 & - 0.0073 w_{12}(T_{r12})^{-8}
 \end{aligned} \tag{108}$$

Their mixture rules are

$$V_{12}^* = \frac{1}{2} (V_{11}^* + V_{22}^*) \tag{109}$$

$$w_{12} = \frac{1}{2} (w_{11} + w_{22}) \tag{110}$$

and $T_{12}^* = 0.85(T_{11}^* \times T_{22}^*)^{1/2} \tag{111}$

for $V_{22}^* / V_{11}^* > 3$

where

$$T_r = T / T^* \tag{112}$$

$$Z_{12}^* = 0.291 - 0.08 w_{12} \tag{113}$$

for pure substance i , ($i = 1$, or 2), w_{ii} , the acentric factor, is defined as:

$$w_{ii} = -\log (P_i / P_i^*) - 1.000 \tag{114}$$

P_i is the saturated pressure of component i at $T_r = 0.7$, and P_i^* is the critical pressure. In an example presented by Prausnitz and Gunn

(34), B_{12} of the mixture of hydrogen and decane calculated by the above equations agrees well with the experimental value. In his calculation, he takes the pseudo-critical properties of hydrogen estimated by Guggenheim and McGlashan (33) and assumes that the acentric factor of hydrogen is zero.

B_{12} of the benzene-helium system at 50°C based on various mixing rules is summarized in Table 14.

Table 14

Comparison of B_{12} of the System Helium-Benzene
at 50°C Computed by Various Mixing Rules

| Arithmetic ^a mean | Lorentz- ^b Berthelot | Guggenheim- ^c McGlashan | Prausnitz- ^{c,d} Gunn |
|---------------------------------|------------------------------------|---------------------------------------|-----------------------------------|
| - 552 ml./mole | 22.5 ml./mole | 24.4 ml./mole | 51.3 ml./mole |

a. Based on $B_{11} = 13$ ml./mole , $B_{22} = - 1123$ ml./mole

b. Based on $C_{11} = 13.07$ ml./mole , $A_{11} = - 2100$ ml./mole , °C²
 $C_{22} = 48.8$, $A_{22} = - 12.8 \times 10^7$ ml./mole , °C²

c. Based on $T^*_{11} = 7.66^\circ\text{K}$, $V^*_{11} = 33.7$ ml./mole , $T^*_{22} = 562.6^\circ\text{K}$,
 $V^*_{22} = 261.0$ ml./mole

d. Based on $w_{11} = 0$, $w_{22} = 0.2196$

Except for the method of arithmetic mean, which is apparently not applicable in a system composed of molecules of widely different sizes, all other methods give B_{12} a relatively small positive value. The Prausnitz and Gunn's rule was chosen in the present study because it has been shown to agree well in the system of hydrogen and decane, which resembles the present system of helium and benzene.

APPENDIX IV

SAMPLE CALCULATIONS

All the calculations were carried out by a Burroughs 220 computer. The procedures and the equations involved have been summarized in the section of the "Procedures of Calculation" in Chapter VI. This sample calculation illustrates the procedures of the numerical calculations.

System Diethylene glycol -- Benzene

Run No. 27

Experimental Data:

V'_{fw} (flow rate of water-saturated helium stream at t_f and P_f): 0.743 ml./sec.

W_2 (total weight of benzene adsorbed in time θ_D): 2.2850 gm.

P_i (pressure at the column inlet): 751.7 mm. Hg

P_o (pressure at the column outlet): 740.3 mm. Hg

P_f (pressure at soap film flow meter): 740.2 mm. Hg

P_s (pressure at the exit of the last saturator): 751.8 mm. Hg

t_f (temperature at soap film flow meter): 32.0°C

t_s (temperature of water bath): 37.6°C

t_l or T (temperature of column): 50.0°C or 323.2°K

W_s (mass of diethylene glycol inside the column): 1.8094 gm.

θ_D (length of the time during which the benzene in the column exit stream was adsorbed by the activated charcoal): 3810 sec.

θ_R (apparent retention time): 401.0 sec.

Calculational Procedures:

- 1) Calculation of the mole fraction of benzene in the mobile gaseous phase, y_2^o :

By substituting the molecular weight of benzene, 78.11 for M_2 in equation (71), the equation becomes

$$y_2^o = \frac{798.4(W_2)(273.16 + t_f)Z_{1f}}{(Q_D)(V'_{fw})(P_f - P_n) + 798.4(W_2)(273.16 + t_f)Z_{1f}} \quad (115)$$

where

$$Z_{1f} = 0.5 + \left\{ 0.25 + B_{11}P_f / [52,363(273.16 + t_f)] \right\}^{1/2} \quad (65)$$

B_{11} was calculated from the constants of the Beattie-Bridgeman equation given by Dodge (51):

$$B_{11} = \left[- \frac{0.0216}{R(273.16 + t_f)} - 0.01400 + \frac{40.00}{R(273.16 + t_f)} \right] \times 10^3 \text{ ml./gm. mole} \quad (116)$$

where $R = 0.08206 \text{ atm.-liter/gm. mole, } ^\circ\text{K}$

From the steam tables of Keenan and Keyes (44), at $t_f = 32.0^\circ\text{C}$, $P_n = 35.7 \text{ mm. Hg}$. By substituting P_n and other experimental data into equation (65), (115), and (116) we obtain

$$B_{11} = 13.54 \text{ ml./gm. mole}$$

$$Z_{1f} = 1.0005$$

$$y_2^o = 0.2184$$

2) Calculation of $(N_m - \bar{G})$

Substituting y_2^0 and other experimental data into equation (72) gives

$$(N_m - \bar{G}) = 0.013995 \text{ moles}$$

3) Calculation of the correction factor for the imperfection of the vapor phase, ϕ

$$\ln \phi = \ln \frac{Z_2^0}{Z_m} - 2(Z_2^0 - 1) - \frac{V_{2L}}{RT} (P_m - P_2^0) + \frac{2P_m}{Z_m RT} (y_1 B_{12} + y_2 B_{22}) \quad (62)$$

$$Z_2^0 = 0.5 + (0.25 + B_{22} P_2^0 / RT)^{\frac{1}{2}} \quad (61)$$

$$Z_m = 0.5 + (0.25 + B_m P_m / RT)^{\frac{1}{2}} \quad (60)$$

where $R = 62,363 \text{ mm. Hg-ml./gm. mole, } ^\circ\text{K}$

B_{22} was calculated by the equation given by Komvzee (30):

$$B'_{22} = 1200 - 90T_A - 6.64T_A^2 + 0.339T_A^3 - 0.0138T_A^4 + 0.0005T_A^5 \quad (117)$$

$$B_{22} = (1 + \frac{B'_{22} P_m}{RT}) B'_{22} \quad (118)$$

where

$$T_A = (T - 320)/10 \quad (119)$$

$$P_m = (P_i + P_o)/2 \quad (75)$$

and

$$T = 273.16 + t_1 \quad (76)$$

B_{12} was obtained by equation (108). The details have been given in Appendix III.

B_m was defined by equation (49):

$$B_m = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \quad (49)$$

where $y_2 = y_2^0$ and $y_1 = 1 - y_2^0$, B_{11} was calculated from equation (116) after substituting t_1 for t_f .

V_{2L} , the volume of liquid benzene, was calculated by the following equation based on the data given by AFI Project 44 (38).

$$V_{2L} = \frac{78.11}{0.01602(55.164 + (15.56 - t_1) 0.000659)} \quad (119)$$

P_2^0 , vapor pressure of benzene at column temperature, is calculated by equation (77):

$$\log P_2^0 = 6.90565 - \frac{1211.033}{220.790 + t_1} \quad (77)$$

The results from the above calculations are

$$B_{11} = 13.18 \text{ ml./gm. mole}$$

$$B_{12} = 51.36 \text{ ml./gm. mole}$$

$$B_{22} = - 1121.7 \text{ ml./gm. mole}$$

$$B_m = - 27.9 \text{ ml./gm. mole}$$

$$P_2^0 = 270.9 \text{ mm. Hg}$$

$$V_{2L} = 88.4 \text{ ml./gm. mole}$$

$$z_2^0 = 0.9847$$

$$z_m = 0.9990$$

$$\phi = 0.9990$$

- 4) Calculation of the activity coefficient, γ_{2L} , and the mole fraction of benzene in the liquid phase, x_2^0 :

Substitute the molecular weight of diethylene glycol, $M_g = 106.12$, and other data obtained in the previous calculations into equations (40) and (41).

$$K_2 = 1.354$$

Substitute the value of K_2 into equation (45)

$$\gamma_{2L} = 3.72$$

The sample size used in this run was 1.0 microliter. Four other samples varying in size from 1.0 to 10.0 microliter were injected in this set of runs at the same experimental conditions. The apparent activity coefficients calculated from the five samples were plotted against sample sizes as shown in Fig. 4 and an extrapolated value of $\gamma_{2L} = 3.78$ at infinitesimal sample size was obtained.

By substituting the value of γ_{2L} at infinitesimal sample size into equation (79), we obtain

$$x_2^o = \frac{\phi y_2^o p_m}{\gamma_{2L} p_2^o} \quad (79)$$

$$= 0.1587$$

APPENDIX V

SOLUBILITY OF BENZENE IN DIETHYLENE GLYCOL

The mutual solubilities of benzene and diethylene glycol have been studied by Johnson and Francis (45). The cloud points versus composition data reported by them were reproduced in Fig. 9. (The compositions which originally were expressed on a weight basis have been converted to a molal basis.) As is illustrated by the three isotherms 50°C, 70°C, 90°C, in Fig. 9, the concentration ranges covered by the present study and that covered by the vapor-liquid equilibrium study made by Pierotti *et al.* (13) are all in the diethylene glycol rich region where benzene and diethylene glycol are completely miscible.

Pierotti *et al.* (13) also reported some experimental data of mutual solubility of benzene in diethylene glycol. Their data are reproduced in Table 15. These data are apparently in error because if their data were correct, most of the vapor-liquid equilibrium data reported by themselves

Table 15

Experimental Solubility Data of Benzene in Diethylene
Glycol Reported by Pierotti *et al.* (13)

| | | | | | | | | | |
|---------------|------|------|------|------|------|------|------|------|------|
| Temp. °C | 107 | 127 | 163 | 187 | 188 | 183 | 161 | 144 | 127 |
| Mole Per Cent | 13.5 | 17.0 | 27.0 | 47.5 | 66.4 | 80.3 | 91.7 | 95.2 | 97.1 |

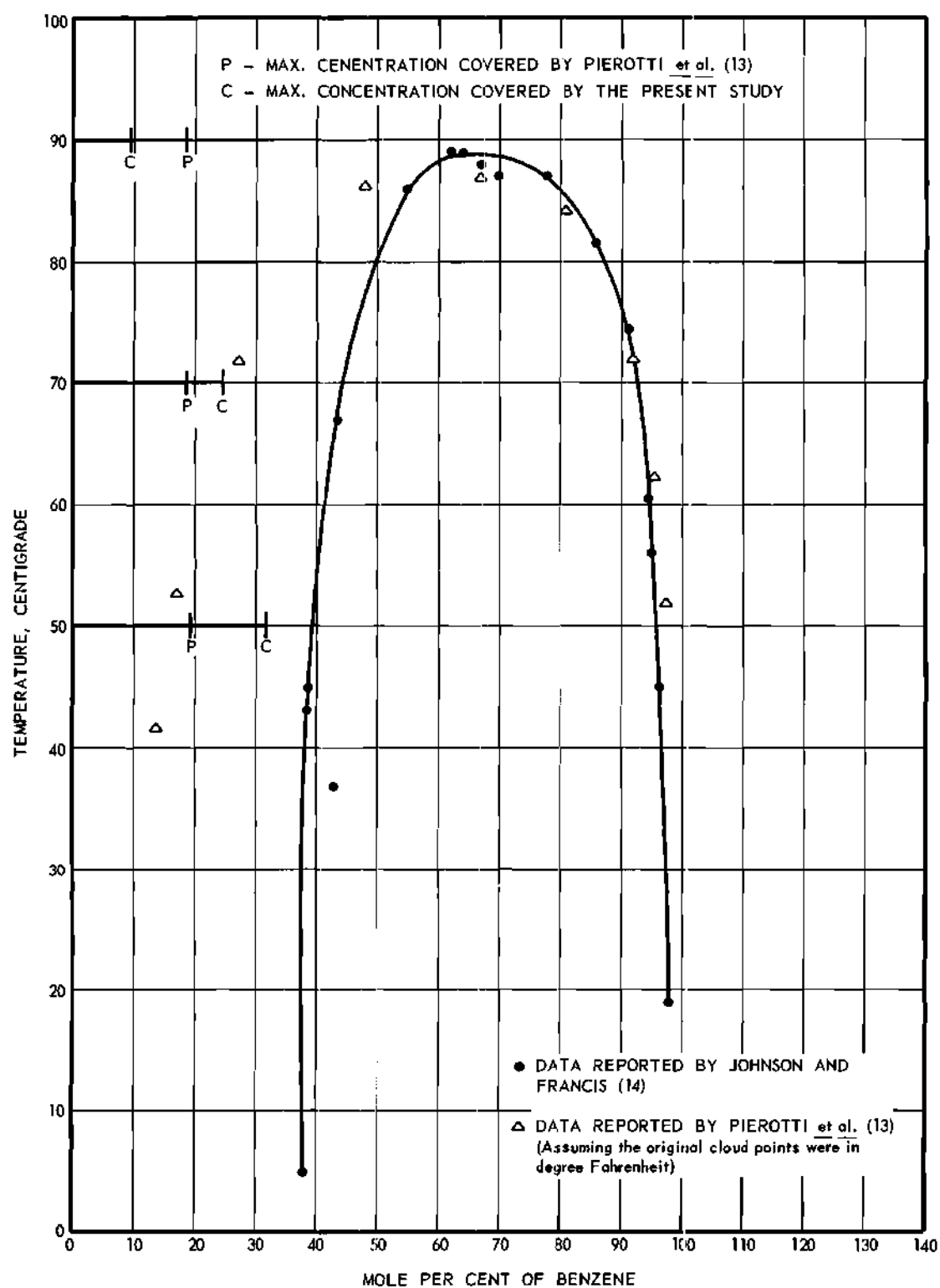


Figure 9. Cloud Points of Diethylene Glycol -- Benzene System.

(13) (see first and fifth columns of Table 7) would be in the two-phase region. In the two-phase region the total pressure should remain constant at constant temperature, but this is in contradiction to what Pierotti et al. (13) have reported. Assuming that the temperature scale of the cloud points in Table 15 was measured in Fahrenheit scale which was misprinted as Centigrade, corrections then were made accordingly and the corrected data were plotted in Fig. 9 to compare with Johnson and Francis' data (45). While the two sets of data agree in the benzene rich region, a great discrepancy appears in the diethylene glycol rich region. Pierotti et al.'s solubility data are doubtful because both their own vapor-liquid equilibrium data (13) and the results obtained by GLC method indicated that at 50°C benzene and diethylene glycol do not form partial miscible phases at benzene concentration of 17 mole per cent as Pierotti's solubility data indicate.

APPENDIX VI

ACCURACY OF THE EXPERIMENTAL DATA

The following quantities, except t_w , and P_s , are the experimentally measured data required to calculate y_2^o , the mole fraction of solute in the vapor phase, γ_{2L} , the activity coefficient of solute in the liquid phase, and x_2^o , the mole fraction of solute in the liquid phase, according to the calculation procedures described in the first section of this chapter. t_w and P_s are needed in the calculation of $(y_2^o)_s$, the mole fraction of solute in the vapor phase of the saturator when the vapor and solute liquid are at equilibrium at t_w and P_s . The purpose of measuring $(y_2^o)_s$ has been discussed in the second section of the "Discussions of the Results" in Chapter VI.

- P_i : pressure at the column inlet, mm. Hg
- P_o : pressure at the column outlet, mm. Hg
- P_f : pressure in the soap film flow meter, mm. Hg
- P_s : pressure at the exit of the last saturator, mm. Hg
- t_f : temperature in the soap film flow meter, °C
- t_s : temperature of the water bath which contained the saturators, °C
- t_1 : temperature inside the column, °C
- W_s : amount of absorbing liquid inside the column, grams
- W_2 : amount of solute adsorbed by the activated charcoal during the time period of Θ_D

V'_{fw} : volumetric flow rate of water-saturated helium gas measured by soap flow meter at t_f and P_f , milliliter per second

Θ_D : length of the time while the solute in the column exit stream was adsorbed by the activated charcoal, second

Θ_R : retention time, second

The experimental accuracy in the determination of each of the measured quantities listed above will be discussed in the following in order to estimate the overall accuracy of the activity coefficients measured by the GLC method.

P_f was the same as the atmospheric pressure which was measured by a barometer. The gauge pressure of P_s was read from a manometer (see Chapter IV, "Experimental Equipment"). Both of the instruments could be read to 0.1 mm. Hg.

Within the flow rate range involved in the present study, the difference between P_s and P_i and the difference between P_o and P_f were found to be less than 0.1 mm. Hg. Therefore, P_i was taken as $(P_s - 0.1)$ mm. Hg and P_o was taken as $(P_s + 0.1)$ mm. Hg, respectively. Such a correction might not be necessary because an accuracy of ± 1 mm. Hg was all required for the measurements of these pressures which were equal or slightly above atmospheric pressure. The ± 1 mm. Hg uncertainty causes an error of less than $\pm 0.2\%$ in the data measured.

The temperature, t_f , was read directly from a mercury thermometer graduated in subintervals of one degree centigrade. The accuracy thus was estimated as $\pm 0.5^\circ\text{C}$. Because t_f appears only in the correction term for the effect of temperature on the gas volume, $\pm 0.5^\circ\text{C}$ uncertainty

causes less than $\pm 0.2\%$ error in the volume measured. t_f also determined the value of P_n , the vapor pressure of the water in the flow meter. At room temperature, a change of $\pm 0.5^\circ\text{C}$ causes less than ± 1 mm. Hg change of the vapor pressure of water. Because P_f in general was on the order of 740 mm. Hg and P_n was in the range of 20 to 30 mm. Hg, an uncertainty of ± 1 mm. Hg of P_n affects less than $\pm 0.2\%$ of the value of $(P_f - P_n)$ which appears in equation (71).

The temperature of the water bath, t_s , was maintained within $\pm 0.05^\circ\text{C}$ by a mercury thermo-regulator. It was measured by a 0.1°C subinterval mercury thermometer which had been compared with an NBS (National Bureau of Standards) certified 0.1°C subinterval mercury thermometer. The temperature of column oven was maintained within $\pm 0.1^\circ\text{C}$ by a thermister controlled electric heater. Column temperature, t_1 , was measured by a copper-constantan thermocouple. It was also calibrated against the NBS certified thermometer. The calibration was fitted by a fourth power orthogonal polynomial equation. The standard deviation of fitted curve values and experimental value is $\pm 0.07^\circ\text{C}$ and the maximum deviation is $\pm 0.15^\circ\text{C}$. By taking into account of the other factor such as the possible uneven distribution of the temperature inside the water bath and column oven, the accuracies of the measurements are estimated to be $\pm 0.2^\circ\text{C}$ for both t_s and t_1 . These temperatures were used to determine the vapor pressure of the solute. According to equations (77) and (78), a change of 0.1°C will cause the change of vapor pressure of benzene of 1.0 mm. Hg at 50°C ($P_2^0 = 271.2$ mm. Hg), 1.8 mm. Hg at 70°C ($P_2^0 = 550.8$ mm. Hg) and 3.42 mm. Hg at 90°C ($P_2^0 = 1020$ mm. Hg) and the change of vapor pressure of n-hexane of 0.67 mm. Hg at 30°C ($P_2^0 = 187.1$ mm. Hg). Therefore,

an uncertainty of $\pm 0.2^{\circ}\text{C}$ gives about $\pm 0.7\%$ error in the vapor pressure of the solute calculated from it.

W_s was weighed to 0.1 milligram. By taking account the possible error in the packing, the accuracy is estimated as ± 0.01 gram or $\pm 0.8\%$ of the total weight of the absorbing liquid inside the column. W_2 was also weighed to 0.1 milligram. By taking into consideration of other possible sources of error, the accuracy is estimated as ± 1 milligram. The total weight of W_2 in general was greater than 1 gram, except in a few cases it was as small as 0.3 gram.

Instead of directly read out as milliliter per second, the soap film flow meter measures the flow rate, V'_{fw} , as the time required for 25.0 milliliter of water-saturated helium gas to pass through the flow meter. The volumetric scale of the flow meter was calibrated by distilled water to an accuracy of $\pm 0.5\%$. The reproducibility of the stop timer in timing the movement of the soap film was ± 0.1 second. The total length of the time for the soap film to move a distance equivalent to 25.0 milliliter volume was in general 30 to 60 seconds, and in no case less than 14 seconds. The accuracy of the flow meter measurement, therefore, is better than $\pm 0.7\%$. The fluctuation of flow rate was found in some cases as much as $\pm 1.5\%$ of the average flow rate. Two or three measurements always made within θ_R while the retention time was measured. An average value was chosen.

θ_R was measured by an electric timer. Major error in the measurement of θ_R was introduced in the determination of the concentration peak point in the recorder chart, especially when a small sample was used. Fortunately, the flat peak generally occurred after a long retention time.

In some cases the uncertainty of the peak point might be as great as ± 5 seconds, the apparent retention time, θ_R , in those cases was always greater than 5 minutes. The error was no greater than ± 1.5 per cent.

Based on the above analysis, all the experimental data are believed to have been measured with an accuracy of ± 1.5 per cent or better.

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